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RESEARCH PAPER RP983

Part of Journal of Research of the National Bureau of Standards, Volume 18, April 1937

CALORIMETRIC DETERMINATION OF THE THERMODYNAMIC PROPERTIES OF SATURATED WATER IN BOTH THE LIQUID AND GASEOUS STATES FROM 100 to 374° C

By N. S. Osborne, H. F. Stimson, and D. C. Ginnings

ABSTRACT

A calorimetric determination has been made of the thermal properties of saturated water, in both the liquid and gaseous states, from 100° C (56 kg/cm²) to the close vicinity of the critical point, 374° C (225 kg/cm²). This new determination supplements a previous determination in this laboratory in the range from 0 to 270° C. With the new apparatus designed and built to withstand severe conditions of temperature and pressure, satisfactory measurements were possible up to within 1 degree of the critical point.

Special tests of the possibility of mixture of the liquid and vapor phases in evaporation experiments indicated freedom from this effect, except within 1 degree of the critical point. These tests included direct measurements of specific volume at 370° C, which confirmed the calorimetric results.

A compilation was made of the thermal properties of saturated water in the interval from 100 to 374° C, giving the vapor pressure and the specific volume, entropy, and enthalpy, or heat content, for both the liquid and gaseous states. This compilation is based on the results of the present measurements, supplemented by data covering the range from 100 to 270° C from the previous investigation. These latter data are in accord with those of the present investigation at the same temperatures.

A number of comparisons between these values and certain groups of similar data from other laboratories are shown graphically.

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I. INTRODUCTION

A program of steam research, sponsored in this country by the American Society of Mechanical Engineers and shared by institutions in other countries, has gone far toward extending and improving steam tables for use in the engineering field. The new data already obtained have been appraised and coordinated by international conferences, thus promoting greater accord among the working steam tables which have been compiled. In addition to fulfilling the original purpose in the service of steam-power engineering, the new data have a wide interest and value in other fields of science, such as chemical thermodynamics, for example.

As its share of the research program, the National Bureau of Standards undertook to determine certain thermal properties of saturated water and steam. The first portion of this project, covering measurements below 270° C (pressure 56 kg/cm^2), was completed and published in 1930. Meanwhile, the use of higher temperatures and pressures in steam engineering has led to a need for extension of the data to higher temperatures, and, for that purpose, a new investigation was begun in this laboratory. Completely new calorimetric apparatus, designed to withstand the temperatures and pressures encountered in the critical region, was built, although, at the time, it was not known how near the critical temperature successful calorimetric measurements could be made.

One by-product of this calorimetric project was a new determination of steam-saturation pressures and a compilation of tables of this property. This compilation was offered as an adjusted appraisal of the available data with the object of encouraging uniformity in steam tables by supplying a factor needed in correlation of steam data.

The present report gives the results of a new series of calorimetric measurements which extend the range of determination of enthalpy of water and steam up to 374° C (225 kg/cm^2). These new measurements also overlap and repeat the part of the earlier series of 1930 between 100 and 270° C.

Especial attention has been given to experiments to give assurance that error was not caused by failure to separate vapor completely from liquid in evaporation experiments. These special experiments included a few direct volumetric measurements as an additional verification.

II. GENERAL DESCRIPTION OF METHOD AND APPARATUS

The essential principles of the method used in the present series of measurements have been developed in previous publications [1].[1] The method has been applied in a previous series of calorimetric measurements [2] completed in 1930, extending up to a temperature of 270° C

[1] The figures in brackets refer to references listed at the end of the paper.

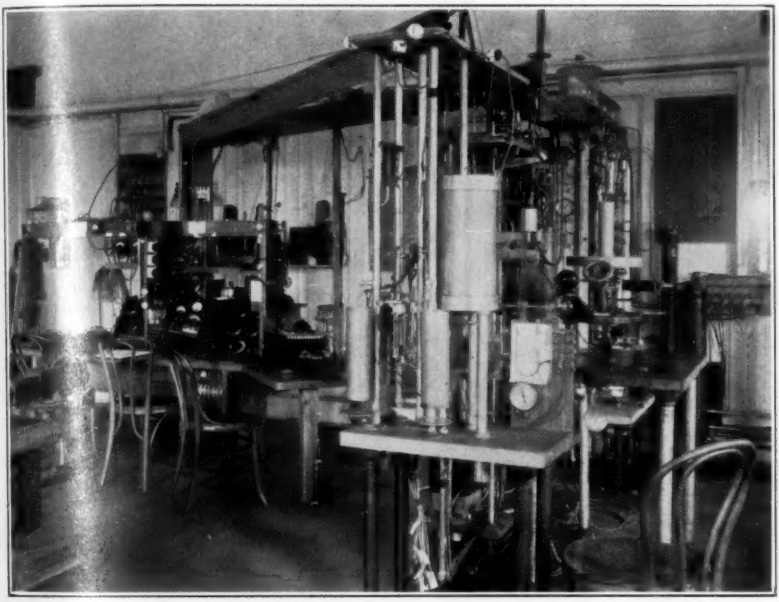


FIGURE 1.—*Assembled equipment.*

The electrical measuring instruments are on the left; the calorimeter is shown at the right.

(56 kg/cm^2). For the higher temperatures and pressures to be encountered in the present investigation up to the critical region, completely new apparatus was built. Partial descriptions of the design of this apparatus and accounts of the progress of the investigation have been published in previous reports [3] from this laboratory. A view of the calorimetric apparatus and of the accessory electrical measuring instruments as set up in the laboratory is shown in figure 1.

Before attempting to describe details of design, construction, and operation, the general scheme of the experimental process will be outlined.

1. METHOD

The method makes use of a single calorimetric equipment with which measurements are made to determine several of the important thermal properties of the saturated fluid. A sample of water in a closed container at some chosen saturation state is heated electrically to some other chosen saturation state, or else is withdrawn either as saturated liquid or as saturated vapor. The energy required for each of these three processes is added and measured electrically. The amount of energy added per unit mass is characteristic of the particular experimental process observed. The group of measurements yields the enthalpy or heat content, together with several other important properties, and establishes the thermal behavior of the saturated fluid in the region covered by the survey.

2. APPARATUS

The apparatus consists essentially of a calorimeter which provides a place where a sample of water may be so isolated from other bodies as to enable its amount, state, and energy to be accounted for. The sample may be made to pass through a chosen, accurately determined change of state, while the accompanying gain or loss of energy is likewise accurately determined. The design of the apparatus provides for several such experimental processes selected for their physical simplicity and for their fitness to exhibit the thermal behavior of the fluid.

A quantity of water, part liquid and part vapor, is inclosed in a metal calorimeter shell. An electric heater immersed in the water provides a means of adding measured energy to the calorimeter system. Outlets with valves provide for putting in or taking out either liquid or vapor. Detachable receivers suitable for weighing are connected to the outlets to hold the samples of water transferred.

For confining the energy, the calorimeter is well insulated from the influence of external sources of heat. In operation, the temperature of an enveloping shell is kept very close to that of the calorimeter shell itself. The residual small amount of heat which passes by leakage to or from the calorimeter system is accounted for.

Means are provided for observing the following quantities:

a. Temperature of the calorimeter and contents.
b. Pressure in the calorimeter.
c. Mass of fluid contents of the calorimeter.
d. Energy added to the system.

The apparatus is designed to permit three special types of measurements to be made. In the ideal case of perfect manipulation and

control of experimental conditions these would consist essentially in observations of the following processes:

1. Heating with fixed amount of contents (heat-capacity determinations).
2. Isothermal expansion by adding heat, evaporating liquid, and removing *saturated vapor* (latent-heat experiments).
3. Isothermal expansion by adding heat, evaporating liquid, and removing *saturated liquid.*

3. RÉSUMÉ OF THEORY OF METHOD

By using the results of the published theory [1], the measured quantities may be expressed algebraically in terms of familiar thermal properties. The experimental determinations of heat capacity of a sample of water give as a result the increase in the quantity,

$$H-Lu/(u'-u)$$

over the observed range of temperature, in which H and L denote, respectively, in energy units, the enthalpy of saturated liquid and heat of vaporization per unit mass, and u and u' denote specific volume of saturated liquid and vapor, respectively.

In the latent-heat experiments we measure the energy which is added when water is evaporated and withdrawn as saturated vapor at constant temperature. This amount of energy per unit mass is equal to

$$L+Lu/(u'-u)$$

The ratio $u/(u'-u)$ is the fraction of a unit mass evaporated but remaining within the calorimeter when unit mass is withdrawn.

The quantity $Lu/(u'-u)$ is complementary both to the determinations of heat capacity and to the latent-heat experiments in the evaluation of H and L. This quantity is measured conveniently at any desired temperature by observing in supplementary calorimetric experiments of the third type the energy required to produce the necessary evaporation when a certain quantity of saturated liquid is withdrawn.

Thus the three different types of experiment yield values of three quantities referred to certain temperatures. These quantities,

$$H-Lu/(u'-u),\ L+Lu/(u'-u),\ \text{and}\ Lu/(u'-u),$$

are denoted by the symbols, α, γ, and β, respectively. From these are derived the values of enthalpy of saturated liquid, H, the enthalpy of saturated vapor, H', and the heat of vaporization, L. In addition to these three characteristic energy quantities, there also may be derived from the calorimetric data the entropies of the saturated liquid and vapor, and by use of the vapor-pressure data, obtained in separate measurements, specific volume and internal energy may be calculated.

The properties of saturated water and steam which may be derived from the calorimetic data, and the formulas by which these derivations are made are as follows:

$$H=\alpha+\beta$$

$$H'=\alpha+\gamma$$

$$L=\gamma-\beta$$

$$\phi=\int\frac{\alpha dT}{T^2}+\frac{H}{T}$$

$$\phi'=\phi+L/T$$

in which the following notation is used:

$$\left.\begin{aligned}\alpha&=H-Lu/(u'-u)\\ \beta&=Lu/(u'-u)=Tu\,dP/dt\\ \gamma&=L+Lu/(u'-u)=Tu'\,dP/dt\end{aligned}\right\}\quad\text{measured quantities}$$

H=enthalpy or heat content per unit mass of saturated liquid $(\epsilon+Pu)$, referred to an arbitrary zero.

H'=enthalpy per unit mass of saturated vapor, referred to the same zero as H.

L=heat of vaporization per unit mass $(H'-H)$.

u=specific volume of saturated liquid.

u'=specific volume of saturated vapor.

t=temperature on international centigrade scale.

T=temperature in centigrade absolute.

ϵ=internal energy per unit mass.

P=vapor pressure at saturation limit.

ϕ=entropy per unit mass of saturated liquid, referred to an arbitrary zero.

ϕ'=entropy per unit mass of saturated vapor, referred to the same zero as ϕ.

The notation used here is that of the previous paper [1] in which the theory of the method was developed. Its retention here is not by reason of any disapproval of the notation adopted by the American Standards Committee but is used to facilitate references to the previous work.

III. APPARATUS

The essential features of the new calorimetric equipment may be explained by reference to a schematic diagram, figure 2. The metal calorimeter shell C contains besides the water sample, an electric heater H_1 and a system of radial silver plates, D, for diffusing heat. This shell is suspended within a thermally controlled inclosure or envelope E, which shields it against heat exchange with the surroundings. Provision is made for withdrawal of either saturated vapor through the vapor throttle valve, VT, or saturated liquid through the liquid throttle valve, LT. The saturated vapor withdrawn passes through a shut-off valve, V, a receiver valve, RV, and is condensed and collected in one of the three receivers, WR, which may be detached at the unions U and weighed. The saturated liquid withdrawn is likewise collected in a receiver WR_1. Provision is made for proper evacuation of all flow lines through vacuum valves, VV. During withdrawal through either the vapor or liquid throttle valve, control of pressure in the calorimeter is accomplished by hand regulation

of these valves, using the differential-pressure indicator *I* to guide the operator. The pressure is transmitted by water through the pressure-transmission cell, *PC*, and glass capillary to a balancing air pressure in air receiver *AR*. The water-air meniscus in the capillary at *I* shows when the pressures are balanced. Temperature measurements at numerous points on the calorimeter shell and its

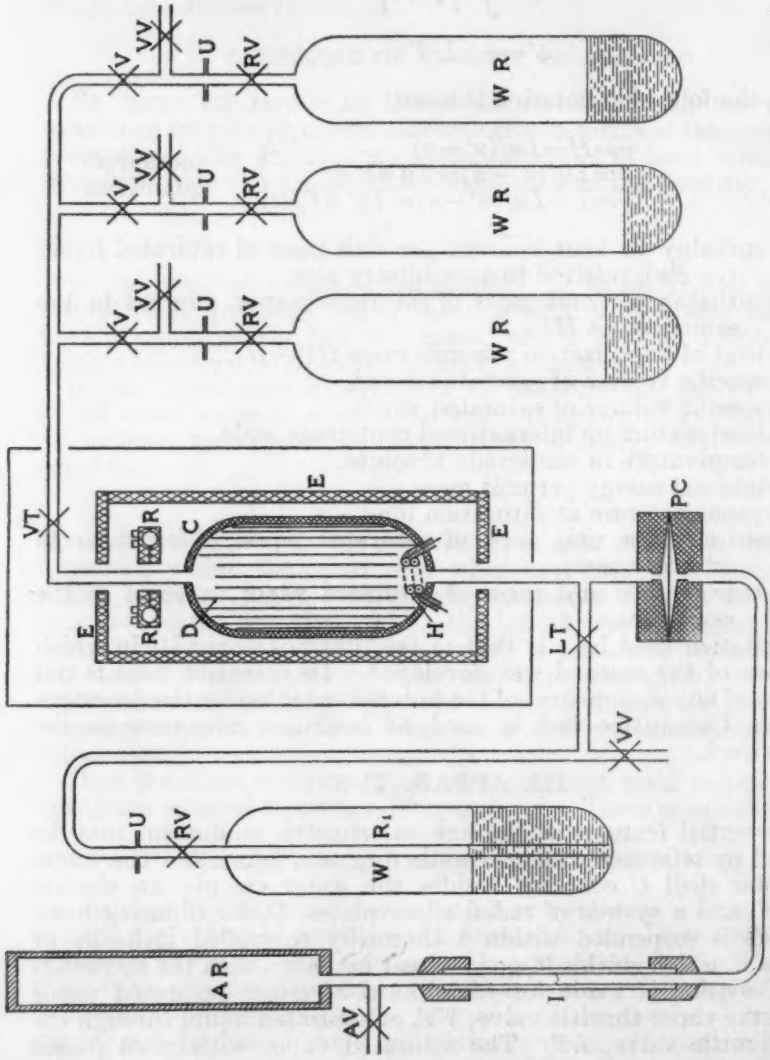
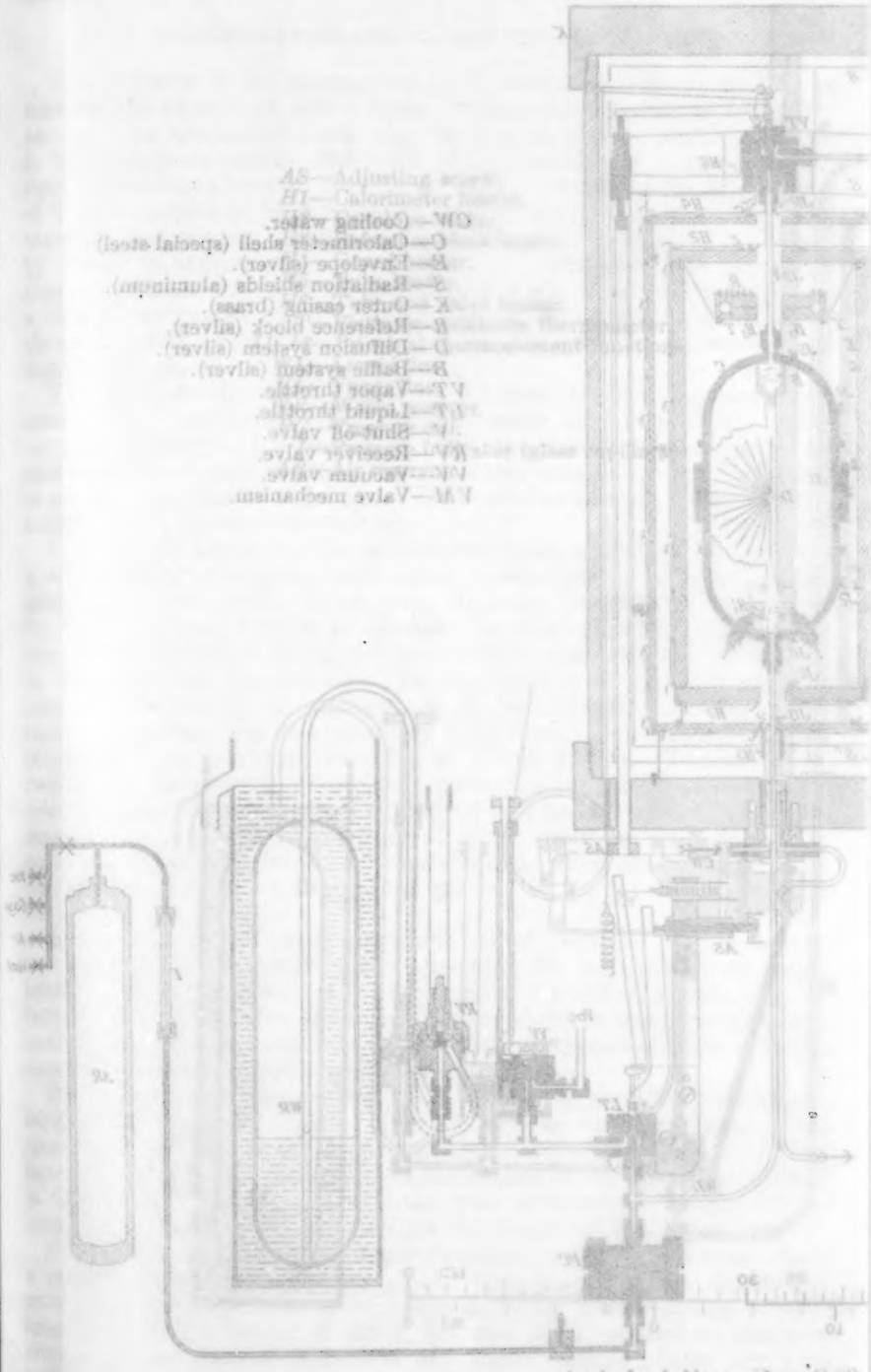


FIGURE 2.—*Schematic diagram of calorimeter equipment.*

C Calorimeter shell.
H Electric heater.
D Heat-diffusion system.
VT Vapor throttle.
LT Liquid throttle.
V Bleeder valve.
RV Reservoir valve.
WR Water receiver.
U Union.
VV Vacuum valve.
I Pressure indicator.
PC Pressure transmission cell.
AR Air receiver.
R Reference block.
AV Air valve.

surroundings are referred by means of numerous thermoelements to a "reference block", *R*, whose temperature is measured by means of two platinum-resistance thermometers. A scale drawing of the assembled apparatus is shown in figure 3. The principal parts will now be described.



AS—Adjusting screw.
H1—Calorimeter heater.
H2—Envelope heater.
H3—Reference-block heater.
H4—Guard heater.
H5—Tube heater.
H6—Tube and valve heater.
T—Platinum-resistance thermometer.
J1, J2—Principal thermoelement junctions.
WL—Liquid line.
VL—Vapor line.
WR—Water receiver.
PC—Pressure cell.
I—Pressure indicator (glass capillary).
AR—Air reservoir.

CW—Cooling water.
C—Calorimeter shell (special steel)
E—Envelope (silver).
S—Radiation shields (aluminum).
K—Outer casing (brass).
R—Reference block (silver).
D—Diffusion system (silver).
B—Baffle system (silver).
VT—Vapor throttle.
LT—Liquid throttle.
V—Shut-off valve.
RV—Receiver valve.
VV—Vacuum valve.
VM—Valve mechanism.

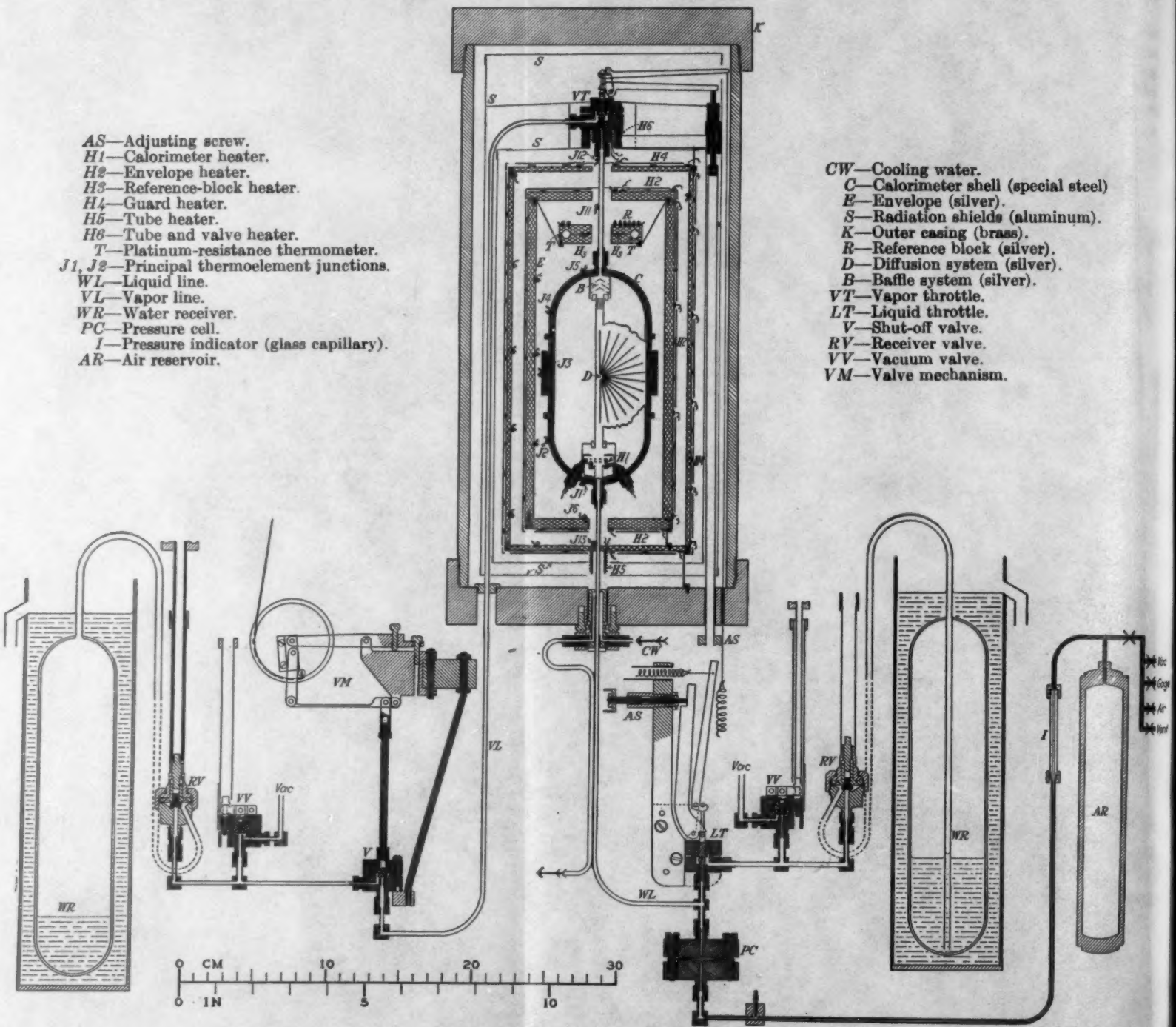


FIGURE 3.—*Section of assembled calorimeter.*

(Note: This is not a true section but shows important parts projected on a plane.)

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1. CALORIMETER SHELL AND INCLUDED PARTS

The purpose of the calorimeter shell shown at *C* in figure 3 is to contain the sample of water while its thermal behavior is being observed. As assembled with the various accessory parts in place, it holds approximately 325 cm^3. The material is a special alloy steel containing about 19 percent of Cr, 7.5 percent of Ni, 4.5 percent of W, 1.3 percent of Si, 0.5 percent of Mn, and 0.46 percent C. This material was chosen because of its resistance to creep and to attack by water at temperatures up to 400° C. The shell was machined from a solid bar and was made in two similar parts held together on a thin silver gasket by the tension developed in the right- and left-threaded band which is screwed on with powerful wrenches engaging machined lugs.

The shell, having a thickness of 3.2 mm, showed no permanent stretch with an internal hydraulic pressure of 4,500 lb/in^2. After carrying a charge of water at 300° C, the inner surface showed on examination no sign of attack by the water other than the formation of a very thin film of light straw color similar to that formed on the outside where in contact with air.

The electric heater in the calorimeter shell, shown at H_1 in figure 3, is an insulated resistor encased in a coiled metal tube sealed hermetically to the shell. It consists of about 10 ohms of calido (Ni, Cr, Fe alloy) wire, 0.2 mm in diameter, with gold leads. This resistor was wound in helical form, 0.6 mm outside diameter and embedded in magnesia for insulation. The magnesia was found to furnish adequate insulation for experiments at the high temperatures. The resistor was sheathed in a platinum tube drawn down tightly on the magnesia to an outside diameter of about 2 mm. This sheathed resistor was then bent to form two turns of a helical coil, 12 mm outside diameter. Each projecting end of this heater was sealed into a threaded plug of silver-palladium alloy by soldering with gold. To complete the seal to the calorimeter shell, the shoulders of these plugs were drawn tightly on thin silver gaskets by threaded nuts outside the shell.

Besides the two main leads which supply current to the heater, two other leads are provided for observing the potential drop in the heater. These potential leads are joined to the current leads midway between the calorimeter shell and the envelope in order to properly include the small amount of energy which is converted to heat in the current leads and transferred to the calorimeter.

The design of this heater was chosen to favor the calorimetric performance of the instrument. The heater was made small to avoid unnecessary heat capacity, to permit operation with small amounts of liquid, and to avoid excessive accumulation of energy as superheat in the liquid. The source of heat was purposely concentrated to cause active boiling and thus induce circulation of the water.

For promoting temperature equalization in the calorimeter shell, a system of heat-conducting plates was provided. A horizontal cross section is shown at *D* in figure 3. This heat-diffusing system consists of 30 flat plates of silver, 0.5 mm thick, shaped to conform closely to the vertical profile of the shell. These plates are held radially in two slotted hubs so as to penetrate and interconnect the space within the shell with a good heat conductor. The function of

this arrangement is to promote temperature uniformity throughout the calorimeter shell and contents.

A baffle system consisting of three conical sheets of silver-wire gauze with passages for steam staggered to prevent direct passage of water drops, is located immediately below the steam outlet as shown at *B*, figure 3. A view of the parts of the calorimeter shell prior to assembly is shown in figure 4.

2. PROTECTING INCLOSURE

The principal purpose of the inclosure which surrounds the calorimeter shell is to oppose heat leak to or from the calorimeter system and to provide for determining the correction for the small unavoidable heat leak. This inclosure consists of two coaxial cylindrical silver shells with flat ends, the inner shell designated as the "envelope" and the outer one the "guard." Pure silver was used for these shells on account of its high thermal conductivity and freedom from oxidation. The envelope is 6.3 mm and the guard 3.2 mm in thickness. Both these shells have electric heater elements properly distributed on their outside walls to permit raising their temperatures uniformly with the mean temperature of the calorimeter surface.

During periods when the calorimeter temperature is kept constant, no current is needed in the envelope heater, but sufficient current is supplied to the guard heater to furnish the heat lost to the outside and keep its mean temperature near that of the envelope and calorimeter. Under these conditions the envelope assumes a nearly uniform temperature, which can be adjusted very close to the mean surface temperature of the calorimeter. The guard temperature can be controlled automatically at any desired constant mean value by means of a sensitive thermoregulator actuated by a platinum-resistance thermometer installed on the inside wall of the guard.

Thermoelements with junctions distributed on the inner surfaces of envelope and guard indicate temperatures to guide the control of heat leak.

In the space outside the guard, two thin aluminum shields are placed to impede the loss of heat from the guard by radiation and convection. Since these shields are only 0.06 mm thick, they do not introduce any considerable lag. Outside the two shields a heavy brass casing, 7 mm thick, serves not only as a cover but also as a protection in case of an explosive failure.

3. CONNECTIONS TO THE CALORIMETER SHELL

The calorimeter shell is held in place by two tubes of silver-palladium alloy. The one at the top bears the weight of the shell and the one at the bottom centers it. Besides furnishing firm support for the shell without too great heat conduction, these tubes serve also for the transfer of fluid to or from the calorimeter. The upper one connects to the vapor-throttle valve, *VT*, which reduces the pressure and permits control of the rate of flow of outgoing steam in the gamma type of experiments. During the alpha experiments which preceded the gamma measurements, the upper tube was temporarily closed by a metal disk in the union at the top of the shell. This suspension tube extends to the calorimeter shell from the body of the vapor-throttle valve, *VT*, which is carried on a light but firm three-arm support from

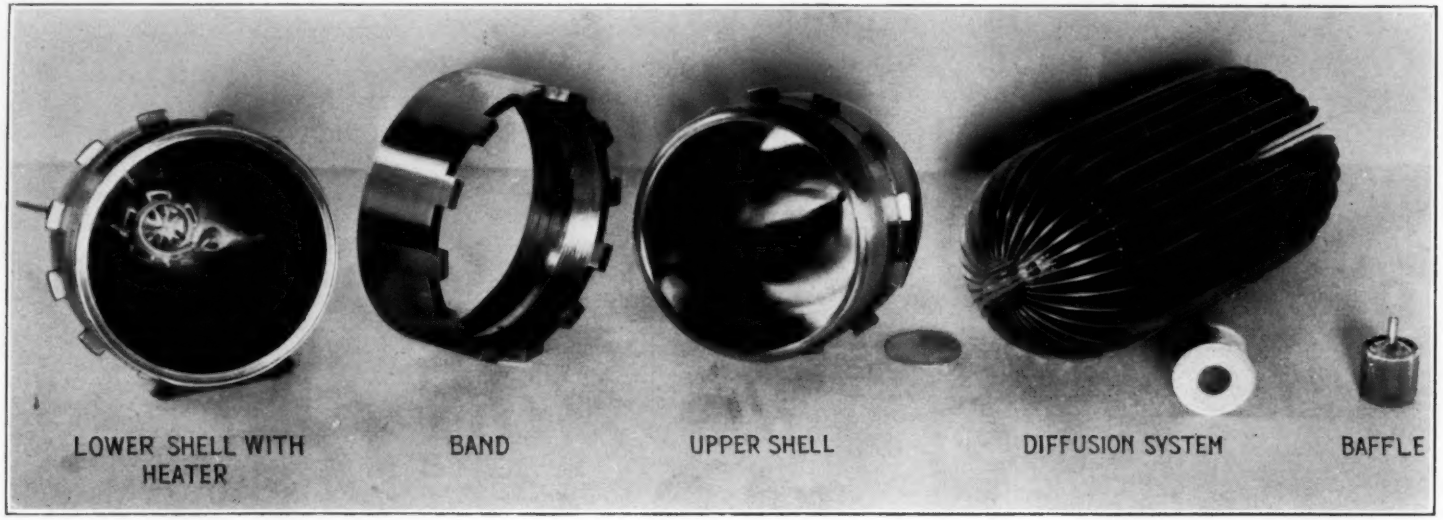

FIGURE 4.—*Unassembled calorimeter shell with accessory parts.*
(One-half actual size.)

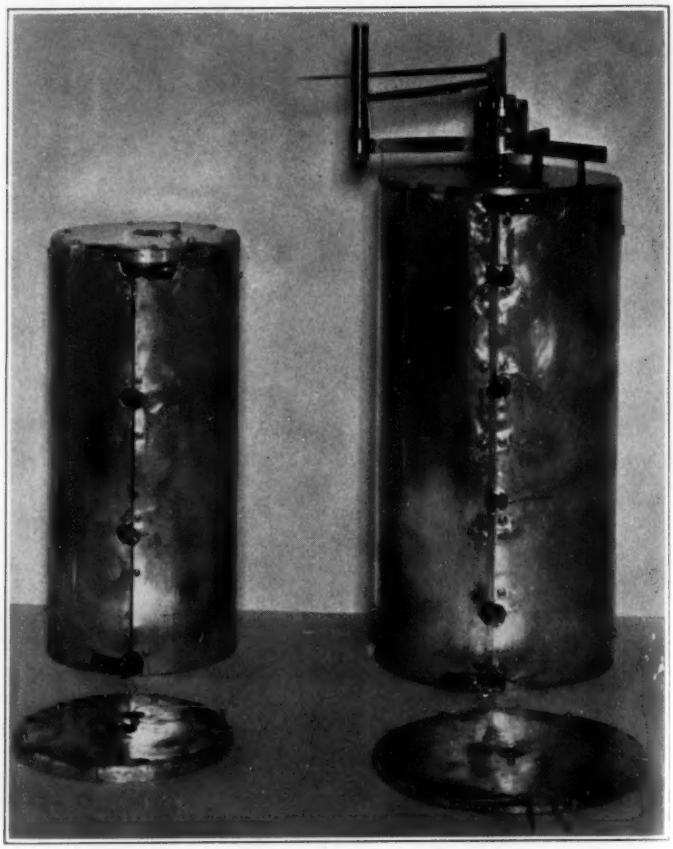

FIGURE 5.—*Silver envelope shells.*

(Envelope on left; guard with vapor throttle on right. One-fourth actual size.)

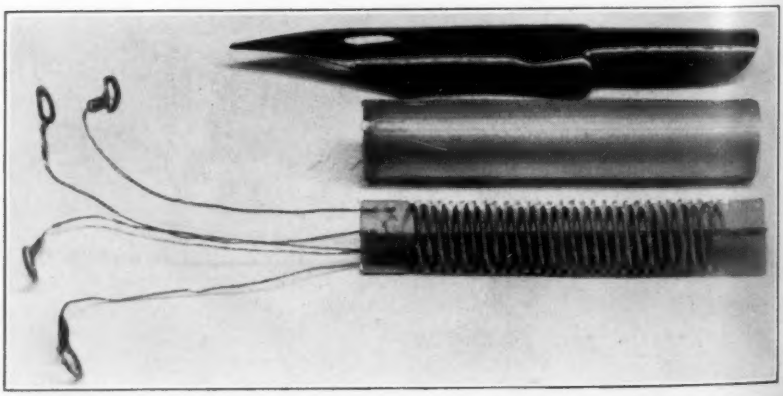

FIGURE 6.—*Platinum-resistance thermometer and sheath, pen point for comparison of size.*

the guard shell. The tube is of 3.0 mm outside diameter with a wall thickness of 0.5 mm.

The lower tube is 2.5 mm in diameter with a wall thickness of 0.4 mm. This tube extends down through a cooling water cell at the level of the brass casing, *K*. Just below this place, the tube ends in a union, not shown in figure 3. From this union an extension leads to a branch point. The two branches connect to the liquid-throttle valve, *LT*, and to the pressure-transmission cell, *PC*. The liquid-throttle valve is used both as a shut-off for the liquid line and also as a means of regulating the rate of flow of liquid in or out of the calorimeter. This valve and the line connecting to the receiver may be immersed in boiling water to drive off water trapped in these parts. The pressure-transmission cell, differential-pressure indicator, and liquid- and vapor-throttle valves will be more fully described later.

Heaters and thermoelements are provided to allow control of temperature gradients on both the upper and lower tubes. For the upper tube the heater is installed on the body of the vapor-throttle valve. The heater for the lower tube is mounted on a cylindrical silver support thermally attached to the tube where it passes through the silver guard shell. There is a free length of the tube of about 2.5 cm between this heater and the union at the calorimeter shell. Below this heater the tube is cooled by means of the water jacket, *cw*, which surrounds the tube at the level of the outer brass casing. The purpose is to establish a definite sharp gradient on the lower tube and also to help cool water when it is withdrawn hot from the calorimeter. It is important to avoid any danger of boiling in the lower tube during experiments, and it is also desirable that the temperature of the emergent portion of the lower tube containing water should not wander erratically.

From the liquid- and vapor-throttle valves, the flow lines lead to the water receivers, *WR*. These receivers are of pure silver of about 425-cm^3 capacity, and are provided with outlet tubes, shut-off valves, *RV*, and unions to permit detaching the receivers for weighing. The receiver valves are of the diaphragm type with differential-thread mechanisms. To facilitate charging the calorimeter with a sample of water, two containers used for that purpose are provided with reentrant tubes reaching nearly to the bottom.

Beyond the vapor throttle the vapor flow line divides into three similar branches, each leading to an automatic shut-off valve, *V*. These valves and the lines immediately connected are immersed in an oil bath heated to a temperature which prevents condensation of vapor ahead of the valves. Experiments had shown that otherwise the distribution of the steam to the containers was erratic. The automatic mechanism for operating these valves by the time signal from the standard clock allows the flow of low-pressure steam from the throttle to be shifted instantaneously from one receiver to another without disturbance of the state of steady flow from the calorimeter. The technique of this operation will be more fully explained later under "experimental procedure."

The three vapor flow lines between the shut-off valves and receivers, and the liquid flow line between the liquid-throttle valve and the receiver, all have branches with valves, *VV*, so that all containers, flow lines, and the calorimeter may be evacuated. Also any small amount of water left after closing the receiver valve may be recovered by condensing in a detachable liquid-air trap in the vacuum line.

4. CONTROL VALVES

The valves used to handle and control the water as liquid and vapor are extremely vital parts. The operator's ability to keep control of the experimental conditions and also to account accurately for the amount of water depends on the nicety with which the valves may be adjusted for throttling or else closed entirely. No effort was spared in the design and workmanship of these valves to make them operate as perfectly as possible. In all of them a flexible silver diaphragm is used instead of packing to seal against the atmosphere and permit linear motion of the stem relative to the seat to open or close the flow aperture. The bodies, bonnets, seats, and clamping screws are all of stainless steel.

The two throttle valves used to control the flow either of vapor or of liquid from the calorimeter, are required to regulate the flow while throttling from the steam pressure down to the receiver pressure so that a steady energy input as heat is just compensated by evaporation of water and a steady state maintained. These differ from the shut-off valves principally in proportions and in the type of closing mechanism.

In all the control valves the aperture in the valve seat is closed by motion of the stem. The end of the stem is faced with an inlaid disk of metal, softer than the seat so that it can conform to the seat and seal tightly. The disk is renewable to allow for replacement when the sealing surface has been eroded. Silver and platinum have both been used for this part, the platinum having been found to resist erosion somewhat better than the silver. The stem has a travel of about 0.1 mm, which is accommodated by the flexibility of the silver diaphragm.

For fine adjustment of the throttle valve setting the stem is moved by end contact with a lever carried on a knife-edge fulcrum and driven by a slow-motion screw giving a large reduction in motion from the screw handle to the valve-stem end. A second lever actuated by tension of a spring takes up backlash or slack motion, and also permits still finer gradual adjustment of the valve setting by hand regulation of the spring tension, thus utilizing the elastic deformation of the valve structure to accomplish the ultimate adjustment.

The several shut-off valves not specially described are similar in principle to the throttle valves, except that the mechanisms used are nonautomatic and nonadjustable for regulation.

5. DIFFERENTIAL-PRESSURE INDICATOR

The differential-pressure indicator has played a very important part in the refinement of experimental technique. By its use, during the flow experiments in which vapor or liquid is withdrawn while evaporation goes on, visible motion of an air-water meniscus enables the operator to observe any slight deviation in pressure and thus allows him to adjust flow to maintain a practically constant pressure throughout the entire period of the experiment. This indicator is only part of a complete pressure-measuring apparatus, which has been described in a previous report [4].

The pressure is transmitted from the free surface of the liquid in the calorimeter through a continuous column of liquid water down to the thin elastic diaphragm of the pressure-transmission cell, *PC*.

The purpose of this cell is to allow the pressure in the calorimeter system to be transmitted to the indicator, *I*, while at the same time preventing the escape of water. Beyond the diaphragm another short water column extends to a balancing air pressure at a boundary meniscus in a glass capillary, *I*. This meniscus indicates the position of the diaphragm in the cell, and is used to show when the pressures on the two sides are balanced.

The transmitting diaphragm is a silver disk, 3 cm in diameter and 0.06 mm thick, stretched flat and clamped near the edge between the two parts of the cell. The diaphragm is most sensitive to changes of pressure when in its relaxed midposition. The cell walls allow a small displacement but never enough to deform the diaphragm beyond the elastic limit, even when the highest pressures used are applied to one side only. The total possible motion of the diaphragm allows a volume displacement of only about 0.04 cm^3 of water from the calorimeter.

The balancing air pressure in the glass capillary, *I*, is kept constant after initial adjustment, by means of an air reservoir, *AR*, immersed in an ice bath in a dewar vessel. The sensitivity of the indicator varies somewhat with the pressure, but, in general, a motion of the meniscus of 1 mm corresponds to a pressure change of about 0.001 atmosphere. The pressure indicator is effectually a sensitive thermometer responding quickly to small changes in temperature of the free evaporating surface in the calorimeter.

6. THERMOMETRIC INSTALLATION

The thermometric installation used in the control and measurement of temperature includes platinum-resistance thermometers and differential thermoelements. Two resistance thermometers installed in a silver reference block furnish a reference datum on the International Temperature Scale from which small temperature differences to the calorimeter or other points may be measured by means of thermoelements. Thermoelements alone are used for the survey of temperature distribution and for regulation.

The reference block was made of pure silver. It was designed to furnish adequate thermal connection between the resistance thermometers and the reference junctions of the thermoelements. The block is made of two similar rectangular pieces of silver, each 5.6 by 3.8 by 0.63 cm, held together flatwise by screws. It is suspended horizontally from the top of the envelope by four slender straps of stainless steel. A hole 12.7 mm in diameter in the vertical axis accommodates the small tube which suspends the calorimeter shell. The two resistance thermometers, *T*, and a pair of electric heaters, H_3, fit snugly into appropriate receptacles machined across the horizontal midsection of the block. These heaters are provided for independent control of the temperature of the reference block.

Two specially constructed platinum-resistance thermometers were used as working standards for the temperature measurement. They were of the four-lead potential-terminal strain-free type described by C. H. Meyers [5].

The windings were made of pure platinum wound on a mica cross and placed in a silver sheath. The type of winding of these thermometers is shown in figure 6. Initial strains were relieved by annealing the completed thermometers at 660° C. The thermometers

were calibrated according to the specifications for the International Temperature Scale [6], which use the fixed points of ice, steam, and boiling sulphur as 0, 100, and 444.6° C, respectively. The thermometers fulfilled the requirements of the specifications for the International Temperature Scale. During the 4 years' use of the two thermometers, they have been calibrated several times and no significant changes were found. One thermometer was used regularly, while the second was used occasionally to check the first. The two thermometers, which were calibrated independently, agreed usually to better than 0.01° C within the temperature range of the experiments.

The thermoelements in the temperature-measuring system are used to survey temperature distribution, to indicate average temperature difference of surfaces, and to determine the temperature of the water sample. Of the 38 principal junctions of the thermoelements, 13 are located on the outer surface of the calorimeter shell, 12 on the inner surface of the envelope, 2 on the upper tube, 1 on the vapor-throttle valve, 3 on the lower tube, and 7 on the inner surface of the guard. The positions of some of the most important principal junctions, J_1, J_2, etc., are shown in figure 3.

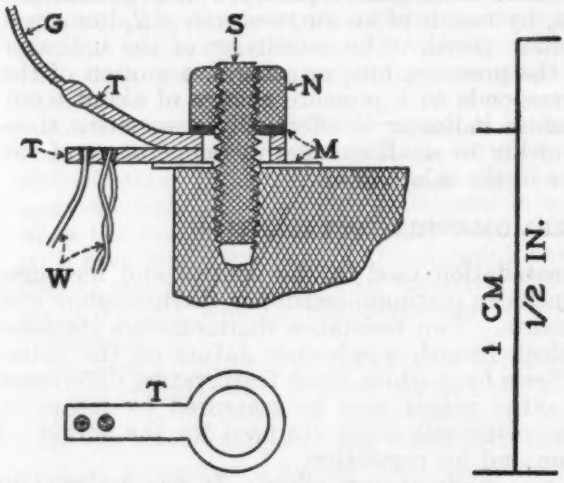

FIGURE 7.—*Details of thermojunction attachment.*

G Gold wire. *S* Stud.
M Mica insulation. *T* Gold terminal.
N Nut. *W* Thermoelement wires.

Each thermoelement is made of 0.1 mm "copel" (alloy containing 55 percent of Cu and 45 percent of Ni) and 0.16 mm "chromel *P*" (alloy containing 10 percent of Cr and 90 percent of Ni) wires, which are threaded through thin strips of mica for insulation and support. A principal junction is made by silver soldering the copel and chromel wires to a tiny gold terminal. Similarly, a reference junction is made by soldering either the copel or chromel to a gold terminal. Other gold terminals connect to gold lead wires. Figure 7 shows how the terminals are installed to secure good thermal connection,[2] electrical insulation, and electrical connection where desired. Additional thermal attachments of the gold lead wires are made at the reference block and at the bottom of the envelope to prevent thermal lead conduction from directly affecting the temperature of the reference junctions. The thermoelements used in the measurement of water temperature were calibrated in place against the resistance thermometers in the reference block. High accuracy in this calibration was not necessary

[2] A diagram showing the details of a thermoelement circuit similar to those used here is shown in a previous paper [2], page 244.

since the thermoelements were used to measure only very small temperature differences.

Various combinations of the thermoelements for the several functions mentioned above are provided by connections to specially built all-copper distributing switches.

By manipulation of these switches the observer can quickly shift from one to another combination, with only the delay for galvanometer response.

IV. EXPERIMENTAL PROCEDURE

In each of the three types of calorimetric experiment there are three principal quantities to be measured, namely, the amount of water subjected to the process, the amount of energy exchanged, and the change in state produced. It is the aim to account accurately for all three of these main factors, either by observations to evaluate separate elements, or by control measures to annul deviations from normal values. The following description of the experimental procedure indicates how these essential accountings were actually made.

1. ACCOUNTING FOR MASS OF WATER

The mass of water subjected to a change of state enters as a direct factor in the reduction of the data. The results, therefore, are no more reliable than the determinations of the masses. Furthermore, in any series of experiments made with a single charge in the calorimeter, a quantitative account of the total mass involved is important evidence concerning the reliability of the data derived from the individual experiments. Equality of the initial amount put in, to the amount taken out in several portions, indicates the absence of gross errors in the observing or recording of weights. Such a sum check was carefully kept in this work and when the accounts did not check properly, the results were discarded.

The general procedure employed in the preparation and handling of the water samples was the same in all types of experiments. A sample of water, purified by preliminary distillation for use in chemical analysis, was redistilled in a specially designed still under a pressure of about 0.1 atmosphere for the purpose of removing dissolved gases. These gases were withdrawn from the condenser together with some water vapor at such a rate that there was but little opportunity for the permanent gases to redissolve in the condensate. Special test experiments showed that this treatment was effective in reducing the residual gas left in the sample to less than 0.001 of the amount initially contained in distilled water. While this redistilled water was not strictly air-free, it was estimated to contain not more than 1/40,000,000 part of air by weight, or in other words, that the partial pressure of the residual dissolved gas in the water sample did not exceed 0.001 atmosphere. This purification was found adequate to avoid any partial pressure of air in the steam which could have a significant effect on the measurements. The purified sample of water was transferred to one of the silver water receivers, which had been evacuated to avoid recontamination with air during the transfer from the still to the calorimeter. Before connecting the water receiver to the water line for charging the calorimeter, the receiver was conditioned and weighed. The conditioning consisted in heating the container valve

to expel any water which was left in the external parts of the valve, then cooling the whole in a current of air from a fan, to the temperature of the room. This treatment was found to bring the receivers to a reproducible condition for weighing, and this routine technique was followed uniformly in loading and unloading the calorimeter in all types of experiments.

All weighings were made by the method of substitution. Corrections were made for buoyancy of the air on the calibrated weights. Correction for buoyancy on the silver container was avoided by using a counterpoise having approximately the same displacement as a container. In addition to the precautions enumerated above, an additional refinement was made in most of the later experiments where higher precision in weighing became more desirable. This refinement was to weigh a dummy silver container at nearly the same time as the silver container containing the sample of water. Since the dummy container was treated in much the same way as the container having the sample of water, the above procedure tended to eliminate possible errors due to changes in condition of surface of the container, changes in the balance arm, and uncompensated changes in air buoyancy.

After weighing, the receiver with its charge of water was attached by a union to the line leading to the bottom of the calorimeter. The calorimeter and line were then evacuated through the vacuum valve until the McLeod gage indicated a pressure of less than 0.001 mm. The system was then considered tight and sufficiently gas-free. The vacuum valve was then closed and the receiver valve opened. The water in the receiver was forced into the calorimeter by its own vapor pressure, using a gas torch to heat the receiver. After the liquid had been driven from the receiver, the calorimeter valve, *LT*, was closed, the valves surrounded with boiling water and the receiver immersed in cold running water. The water remaining in these connecting lines was thus distilled back into the receiver, which was then shut off and detached. Experiments showed that after this operation the vapor left in the lines was negligible in amount.

The receiver was then conditioned and weighed again to give the tare for determining the net charge introduced into the calorimeter system.

After a series of experiments in which part of the charge of water may or may not have been withdrawn, the water remaining in the calorimeter was withdrawn into the container. This was done while the calorimeter was hot, thus leaving the calorimeter and its outflow tube dry. After distilling the remainder over to the container and closing the container valve, the residue of vapor still left in the calorimeter could be recovered by condensing in a liquid air trap in the vacuum line. It was found, however, that this residue was very small and so uniform in amount that it need not be determined for each emptying. The final comparison of the masses in and out of the calorimeter was found to be an adequate check on the technique of determining the mass of water.

2. ACCOUNTING FOR ENERGY

Measured energy was supplied electrically to the calorimeter and contents by means of the calorimeter heating coil installed within the calorimeter shell and immersed in the water sample. Power was supplied by a separate 30-volt storage battery of large current capacity. A Wolff-Diesselhorst potentiometer was used for measurements of

current and potential drop in the heater. A 0.01-ohm four-terminal resistance in series with the heater was used for the current determination, and a ratio volt box for the potential drop. Correction was made for the fraction of the main current shunted through the volt box. In order to avoid too rapid initial change when the current was switched to the calorimeter heater at the start of an experiment, a dummy or spill resistance was used to steady the battery output. The shift was made instantaneously by means of a double-pole double-throw switch which was automatically actuated by the electric seconds signals furnished by the standard clock. The heating periods were usually an integral number of minutes and there was no significant error in the time measurement (probably less than 1/50,000).

In one type of the gamma experiments, the time signals were used in a similar manner to actuate the shut-off valves which shifted the flow of steam from one receiver to another while the electric power input to the heater was uninterrupted. The energy supplied to the calorimeter while a given sample was being withdrawn was then calculated for the period thus determined.

All electrical measuring instruments were carefully calibrated at this Bureau. The potentiometric measurements of power input were referred to any one of a group of three cadmium standard cells. These cells were of the saturated type and were maintained at a constant temperature in a special temperature-control box described by Mueller and Stimson [7]. Frequent calibration of the standard cells proved their reliability.

In an ideal calorimetric experiment, only the energy supplied electrically to the calorimeter would need to be considered. In practice, the ideal of absolute thermal isolation of the calorimeter from the surroundings is never quite possible. In these experiments the thermal leakage was not negligible, yet it was made small by instrumental and experimental precautions, and this remaining heat transfer, which was usually about 0.01 percent of the total energy, was determined with the necessary precision for use as a correction term.

The actual heat-leak correction was evaluated with the aid of numerous differential thermoelements which indicated temperature differences between points on the calorimeter and points on its immediate surroundings. These temperature difference indications were observed every minute and summed algebraically to give integrated heat-leak factors. These factors when multiplied by heat-leak coefficients determined in special experiments, gave the heat-leak corrections. In these special experiments the temperature change in the calorimeter and contents was observed when the surroundings are controlled for a definite period of time at a known exaggerated temperature difference from the calorimeter. Knowing the approximate heat capacity of the calorimeter and contents, its temperature change could be reduced to actual heat transferred, and the heat-leak coefficients evaluated. In this investigation, the heat leaks are classified into four types. They are designated as "envelope heat leak", "top heat leak", "bottom heat leak", and "residual heat leak."

The envelope heat leak occurs when the envelope, or metal surface immediately surrounding or opposed to the surface of the calorimeter, differs from it in temperature. Twenty-three thermoelements distributed appropriately on these surfaces integrated their surface

temperatures and when properly connected indicated the average temperature difference.

In actual experimental conditions, the average temperature of the envelope could be regulated very close to that of the calorimeter shell. This nice temperature regulation of the envelope was effected directly in the first or alpha type of experiment (heat-capacity determinations) by use of the electric heater on the envelope. In the constant-temperature experiments of the second and third types, the regulation was maintained by automatic control of the temperature of an outer shell or "guard."

The top heat leak is due primarily to the heat conduction along the tube connected to the top of the calorimeter. After piercing the disk in this tube to provide for the gamma experiments, it was necessary to keep this tube slightly warmer than the calorimeter in order to avoid the possibility of condensation of water and transfer of unmeasured heat from the calorimeter system. This caused a small flow of heat toward the calorimeter, which was evaluated in terms of the temperature gradient in the tube as indicated by thermoelements. Temperature control of the upper part of the tube was effected by use of a special electric heater in two sections attached to the vapor-throttle valve. This heater also provided for compensating the cooling which occurred in the throttle valve when reducing the pressure of flowing steam in latent-heat experiments.

The bottom heat leak is analogous to the top heat leak with the difference that the lower tube is kept colder than the calorimeter to avoid the possibility of boiling in the lower tube with transfer of unmeasured heat to the calorimeter. It was evaluated in like manner, and the temperature of the lower part of the tube was controlled by a special electric heater, thermally attached.

The fourth type of heat leak is called "residual" because it still exists when the other three have been annulled. In other words, it is a measure of the heat gained or lost by the calorimeter when every known precaution against such a heat transfer has been taken. The value of this heat-leak rate was determined by means of blank experiments in which no electric energy was supplied. The other three heat leaks were controlled and corrected for. During the course of the gamma and beta measurements, about 300 separate determinations were made of this residual heat-leak rate. A study of these determinations by a semigraphic analysis showed that, while this rate was so small as to be nearly insignificant, yet it was definite enough to warrant applying corrections. Although the cause of this residual heat leak was unknown, these corrections were applied to all gamma and beta measurements to remove, as far as possible, this source of systematic error.

All four types of heat leak varied with temperature, and the coefficients were checked frequently during the experiments throughout the range of temperature.

3. ACCOUNTING FOR CHANGE IN STATE

Two means are available for evaluating the change in state of the sample of water, namely, measurement of either temperature or pressure. Either is suitable as an independent coordinate for expressing the properties of saturated steam, and convenience determines the choice practically.

Independent measurements have now established the characteristic relation between temperature and saturation pressure of steam with satisfactory accuracy in the range of the present measurements. Pressure observations were therefore unnecessary in the calorimetric measurements, except as they were used to indicate the state at which evaporation proceeded and thus enable the operator to control that process by hand regulation of the throttle valves. For determining the initial and final state of water in the calorimeter, temperature measurement was used entirely.

The temperature of the water in the calorimeter, when in equilibrium, was measured by the two platinum-resistance thermometers, used in conjunction with thermoelements, as previously described. The temperature change of the calorimeter and contained water sample was thus accurately observed in all experiments. All observed temperatures are expressed on the International Temperature Scale.

For determining either the initial or final temperature, each temperature reading consisted in simultaneous observations of resistance thermometer and thermoelements. The five thermoelements having principal junctions designated J_1 to J_5, inclusive, were connected in series to indicate the mean temperature of the calorimeter with respect to the reference block. Four successive temperature readings were made at equal time intervals. This method of reading several successive temperatures is desirable for several reasons. The four-lead potential-terminal resistance thermometer requires at least two observations to eliminate the lead resistance from the measurement. Increasing the number of readings decreases the accidental error of observation. A regular schedule of readings takes account of slight drift of temperatures.

Provision is made for observing by differential thermoelements any deviation in temperature of steam or water withdrawn, from the initial saturation temperature, so that correction could be made, if required, for this change of state.

In actual experiments it was found that the steam left the calorimeter at the saturation temperature as closely as could be observed, so no correction need be applied. In the beta experiments when liquid water was withdrawn it was found that the correction was appreciable, although small.

In both the gamma and beta experiments, the first where vapor is withdrawn, the second where liquid is withdrawn, the control of the pressure to constancy is an important part of the accounting for the state of the fluid. The technique of this operation deserves special mention. The differential-pressure indicator (previously described) was extremely sensitive, particularly at the higher temperatures for which this instrument was expressly designed. The special throttle valves, by which the operator regulated the flow to keep a constant evaporation temperature, have proved amazingly delicate, and have enabled the operator to maintain a control which was practically perfect. This technique, therefore, made it possible to run the evaporation at the initial calorimeter temperature so that no corrections were necessary for changes in evaporation temperature.

A change in the distribution of liquid and vapor in the calorimeter occurs in all three types of experiment. This change is analyzed in the theory of the method, and is accounted for by use of the quantity

which is designated as beta. This quantity was determined calorimetrically throughout the range above 200° C.

Special details of experimental procedure which apply to the particular types of calorimetric measurements will next be described. These measurements were performed in a manner similar to those described in previous reports, save for differences peculiar to the apparatus or to the experimental range.

4. DESCRIPTION OF ALPHA EXPERIMENTS

It will be recalled that these experiments yield values of the change with temperature of the quantity, $H-Lu/(u'-u)$, denoted by the symbol α. Combined algebraically with values of $Lu/(u'-u)$ obtained from independent measurements, the data suffice to determine the change in enthalpy of the saturated liquid, H.

The procedure in these alpha experiments consisted essentially in heating a sample of water, part liquid and part vapor, over an accurately measured temperature range, and accounting for the energy added in the process. Two such heat-capacity determinations, a gross and a tare, are required for an evaluation of the change in α. These two determinations over the same temperature interval are made with different charges of water always maintaining the saturation condition. The one made with a large charge yields a gross value of energy added. The other, made with a small charge, yields a tare value. The difference or net value of energy added, divided by the net mass gives the value of the change in α for that temperature interval. This method of differences avoids the necessity of determining the heat capacity of the empty calorimeter.

The actual experiments were not limited to a single pair of measurements, but for each temperature interval, a group of measurements was made with several different charges of water, including both large and small charges. Two series of such groups were made, one in 10-degree intervals between 100 and 370° C, and another in 50-degree intervals between 100 and 350° C.

During the alpha experiments, the calorimeter was closed from connection with the upper tube by a metal diaphragm in the union at the top of the calorimeter, to avoid possible error from condensation of water in the upper tube.

Certain peculiarities characteristic of the behavior of the water sample in attaining thermal equilibrium at the higher temperatures have been noted in the previous report on vapor-pressure measurements made in this same apparatus. On account of this behavior there is a decrease in precision in accounting for the state as the critical region is approached. The results are also less precise in this region on account of the decrease in the net mass of water available when keeping the necessary saturation conditions. Greater tolerances are therefore unavoidable in the extreme upper range.

5. DESCRIPTION OF GAMMA EXPERIMENTS

These experiments yield values at a given temperature of the quantity, $L+Lu/(u'-u)$, denoted by the symbol γ. Combined algebraically with corresponding values of β, i. e., $Lu\ (u'-u)$, the data suffice to determine the heat of vaporization, and thus complete the evaluation of the enthalpy, H', of saturated vapor.

The procedure in these gamma experiments consists essentially in removing a definite mass of saturated vapor from the calorimeter at a constant temperature, and accounting for the energy added in this process. The disk which closed off the calorimeter at the upper union in the alpha experiments was punctured to allow passage of steam out the top.

Two different procedures were used in separate series of determinations, as an additional check on possible causes of systematic error. In one series, designated as method *A*, a number of successive determinations at a given temperature from a single charge of water were conducted as a continuous experiment. The evaporation and withdrawal of vapor were conducted as a steady process without interruption, but divided into separate determinations by directing the flow of vapor successively into different receivers. In this method the initial and final conditions in the calorimeter for each determination were evaluated with the process taking place at a steady state but not in a state of equilibrium.

In the other series, designated as method *B*, each determination was conducted as a completely separate experiment, starting and stopping with equilibrium prevailing in the calorimeter. The measurements made prior to March 23, 1934, were by method *A*, those after that date by method *B*. Each method has its advantages and disadvantages, but the results, where they could be compared with each other and with the results of the earlier measurements made with a different calorimeter, did not show any significant systematic difference as a result of either different manipulation or different apparatus.

Considerable investigation was made at high temperatures of the effect of the rate of withdrawal on the results of the experiments. It is reasoned that if liquid drops were entrained with the steam as a result of active boiling, the degree of wetness would be expected to increase with the rate of evaporation and with approach to the critical region. For this reason the rate of withdrawal was varied over a wide range in different experiments, especially at the higher temperatures where the effect should be greatest. No significant change in the results was obtained except near the critical temperature.

6. DESCRIPTION OF BETA EXPERIMENTS

To complete the determinations of heat content, H, from the results of the alpha experiments, and of heat of vaporization, L, from the gamma experiments, it is necessary to know the values of the quantity, $Lu/(u'-u)$, denoted by the symbol β. This quantity, which enters into the reduction as an insignificant correction term at 0° C, increases in magnitude with rising temperature, until at the critical state its limiting value becomes equal to that of gamma, when the heat of vaporization becomes zero.

It is shown in the theory [1] that beta may be determined calorimetrically as the amount of energy required per gram of saturated liquid withdrawn to just balance the heat expenditure in the evaporation which takes place in this process. Beta may also be determined by calculation, using the specific volume of the saturated liquid and the derivative of the vapor pressure in the formula, $\beta = Tudp/dt$. In fact, now that the specific volumes of liquid water have been determined

with such precision by Smith and Keyes [8] at Massachusetts Institute of Technology, it is only in the range of higher temperatures that the calorimetric method is comparable in precision with the direct volumetric measurements. As a part of the complete calorimetric program the measurements of beta were made and values obtained in the range from 100 to 374° C. These measurements were found to be confirmatory of the MIT smoothed-volume data, with the exception of small departures above 330° C. These beta measurements, together with dp/dt, constitute an independent evaluation of liquid specific volume, as well as a factor in evaluating the enthalpy.

The determination of beta was similar to a determination of gamma by method *B*, starting the flow and completing the experiment with the state of equilibrium prevailing in both cases. The essential difference was that liquid was withdrawn from the bottom of the calorimeter instead of vapor from the top. Regulation of the flow by a sensitive throttle valve was guided by the pressure indicator as before, to maintain constant evaporation temperature in the calorimeter. With careful attention given to the regulation of this valve, particularly at the beginning and end of the flow, it was possible to avoid any disturbance of the desired steady conditions sufficient to cause significant error.

Since it might be supposed that steam bubbles could be entrained in the withdrawn liquid, especially when near the critical region, tests were made of the effect of rate of withdrawal on the results in the same way as was done in the gamma experiments. Here again, no positive effect was observed which could be attributed to rate.

V. RESULTS OF MEASUREMENTS

The principal data from the three types of calorimetric experiments are given in tables 1, 2, and 3. (See pages 432, 437, 439.) These tables contain only the data remaining after sifting the record and discarding all experiments which were of doubtful worth on account of defects in the experimental technique. Examples of such defects were cases where fluid leaks occurred, where mass determinations failed to check properly, or where heat-leak control was faulty or the record deficient.

All known corrections for instrument calibrations and preliminary reduction of actual observed quantities have been made prior to these tabulations, which omit details of the complicated and bulky record of original observations. Further reduction and formulation of the results are next described.

1. REDUCTION AND FORMULATION OF DATA FOR ALPHA

From the alpha measurements, a group of data was obtained for determining the energy used in heating the calorimeter and its charge of water in each individual experiment. These data, corrected for instrument calibrations and for the several heat leaks, previously mentioned, are listed in table 1 as "Entire energy added." The four heat-leak corrections are combined and listed as "Heat leak." Since the values of entire energy are those for the actual measured increments of temperature, and since these differ slightly from the even values intended, the energy values were next adjusted by interpolation to correspond with the even temperatures at the 10-degree points. The values of $[Q]_1^2$ thus obtained were then ready for reduc-

tion to determine the change in alpha with temperature, $[\alpha]_1^2$, as a step toward deducing the change in enthalpy. The method of making the further reductions by deducing a calorimeter calibration from the experimental alpha data will next be described by starting with the general equation for constant mass or alpha experiments.

Taking account of the liquid in the lower tube below the calorimeter, the equation may be written

$$[Q]_1^2=\left[E_A-VP+V\frac{L}{u'-u}+(M-m)\alpha\right]_1^2$$

in which $[Q]_1^2$ denotes the energy added to the calorimeter and its contents in heating through the even temperature interval, t_1 to t_2, in a single experiment; M is the total mass of the charge introduced into the calorimeter system; m is the mass of the small portion (less than 0.5 percent) of the total charge in the connecting line outside the calorimeter boundary; E_A is the internal energy of the calorimeter; V is the internal volume of the calorimeter; P is the internal pressure; L is the heat of vaporization; and u' and u are specific volumes of saturated vapor and liquid, respectively; α is the specific property of saturated liquid water denoted by $H-\frac{Lu}{u'-u}$, where H is enthalpy of saturated liquid.

In this expression, the increments of temperature and the amounts of the charge are the independent variables, the resulting values of $[Q]_1^2$ are determined, as described above, from the observations.

Letting

$$\left[E_A-VP+V\frac{L}{u'-u}-m\alpha\right]_1^2=[Z]_1^2,$$

the values of $[Z]_1^2$ or ΔZ are found from the sets of observations for each temperature interval by simple least-square solutions of the resulting equations of the form

$$[Z]_1^2=[Q]_1^2-M[\alpha]_1^2$$

The values of ΔZ from the 10-degree intervals were next adjusted by smoothing them with respect to temperature.

(This adjustment of the ΔZ's was facilitated by separating each value into two parts. By rearranging, the above equation may be written

$$[Z]^2_1=[E_A-m\alpha]^2_1+\left[V\left(\frac{Tdp}{dt}-P\right)\right]_1^2$$

In this form, the last term contains quantities which are known with considerable accuracy and are relatively free from irregularities. This term was computed separately for each set of data and the values subtracted from the ΔZ's. The part which remained was found to vary by only about 10 percent and almost linearly over the entire range of temperature. Since the heat capacity of the empty calorimeter makes up over 99 percent of this term, and since the material

of the calorimeter is known to have no abrupt transformations in the temperature range used, it is proper to adjust the experimental values by smoothing. A simple formulation of these values smoothed out accidental irregularities. The corresponding values of $\left[V\left(\frac{Tdp}{dt}-P\right)\right]_1^2$ were then restored to these smoothed values to give the smoothed values of $\triangle Z$ for each temperature interval. By this method of reduction and smoothing, there is deduced a calibration of the calorimeter as actually used in accordance with the theory. This calibration is analogous to the usual calorimeter calibrations for heat capacity, differing, however, in that the function ΔZ includes more than the mere heat capacity of the empty calorimeter.) These smoothed values of ΔZ are given as $[Z]_1^2$ for each 10-degree interval in table 1.

Using the adjusted values of ΔZ, each experiment now becomes a measurement of $\Delta\alpha$. The general equation may now be written

$$\Delta\alpha=[\alpha]_1^2=\frac{[Q]_1^2-[Z]_1^2}{M}$$

The values of $\Delta\alpha$ calculated thus are listed in table 1. It is evident that although experiments with both large and small charges are necessary in order best to evaluate ΔZ, the values of $\Delta\alpha$ from these low fillings are, in general, inferior in precision to those from larger masses. This is taken into account in calculating the mean values of $\Delta\alpha$.

The data from the 50-degree intervals, included in table 1, were made in two groups, designated as *I* and *II*, both of which were made earlier and with less perfect experimental technique than the measurements in 10-degree intervals. The summed heat-leak corrections were not applied to group *I* because of known causes of error in their evaluation. These errors would tend to balance out in the determination of $\triangle\alpha$, but not in the determination of ΔZ. Furthermore, some minor repairs made on the calorimeter after group *II* probably made small changes in the heat capacity and, therefore, in the ΔZ. For these reasons the measurements of groups *I* and *II* were calculated directly without using the adjustment of ΔZ applied to the 10-degree intervals.

The results of the determinations for the two 50-degree groups were then combined with assigned weights to be included with the data from the 10-degree intervals. In the final assembly and formulation of α, groups *I* and *II* do not greatly affect the final result. They do, however, comprise an independent though somewhat inferior series of measurements, which may be compared with the accepted formulation.

In addition to the measurements made with the present calorimeter and described above, other data were available in the interval of 100 to 270° C from observations made with the previous calorimeter and published in 1930. Since these independent data were in the same range as the later ones, they also were included in the revised and extended formulation made possible by the present new group of results. This formulation of the entire group of data for α will next be described.

The empirical equation deduced to represent smoothed and adjusted values of the increment of α, $[\alpha]^t_{100}$, from the 100° point to any temperature, t, may be written

$$\alpha]^t_{100}=A(t-100)-B(t^2-100^2)-C\int^t_{100} 10^{-Dt^2}dt$$

where

$$A=4.349321 \qquad B=4.23834\times10^{-4}$$
$$C=0.153528 \qquad D=0.208103\times10^{-4}$$

α is in int. j/g and t is in degrees centigrade. Values of α calculated by this equation are given in table 5 (see page 444), taking the value of $[\alpha]_0^{100}$ as 417.36, as previously determined in this laboratory [2].

Figure 8 shows graphically the values of the derivative $d\alpha/dt$, calculated by means of the above equation and plotted with respect to temperature. For comparison the values from the 1930 formulation, and the values as derived directly from the adjusted experimental data are shown. Figure 9 shows a graphical comparison between the values of $[\alpha]^t_{100}$ from the different groups of measurements and the accepted formulation. This shows the accord of the separate series of measurements made at different times with different technique or different apparatus.

2. REDUCTION OF DATA FOR BETA AND GAMMA

The β and γ experiments were very similar in principle and with few exceptions, the reduction of the data was the same for both. The reductions for β will be first described.

Data were obtained from the β experiments for determining the energy used in the process of withdrawing saturated liquid from the calorimeter at a steady state. The measured electric energy added to the calorimeter was first corrected for electric-instrument calibrations and then for the several heat leaks previously mentioned. Although the corrections for residual heat leak were small, they were applied because systematic. Still another correction was applied to account for the small difference of the final temperature of an experiment from the initial temperature. This correction is for the energy which would bring the calorimeter and its contents, M_2, at the end of an experiment, back to the initial temperature. The technique of the experiments was such that the change in temperature, Δt, was usually small. The corrections, ΔQ, were calculated by use of the equation

$$\Delta Q=\left(\frac{dZ}{dt}+M_2\frac{d\alpha}{dt}\right)\Delta t,$$

taking the values of dZ/dt and $d\alpha/dt$ as determined in the alpha measurements. In a few of the later experiments, observations and corrections were made for a further small amount of energy caused by the transfer of a few milligrams of water between the calorimeter and the differential-pressure indicator. Since this correction is proportional to the mass so transferred and to the value of β, it is significant only when β is large. The values of these combined corrections to the entire energy added are listed as "Energy Corrections" in table 2. After applying these corrections to the observed data, the corrected values are listed as "Entire Energy Added."

The entire energy added was then divided by the mass of fluid withdrawn to give the energy added per gram, which is approximately equal to β. In most of the β experiments, it was necessary to correct this approximate value for the superheat of the liquid withdrawn.

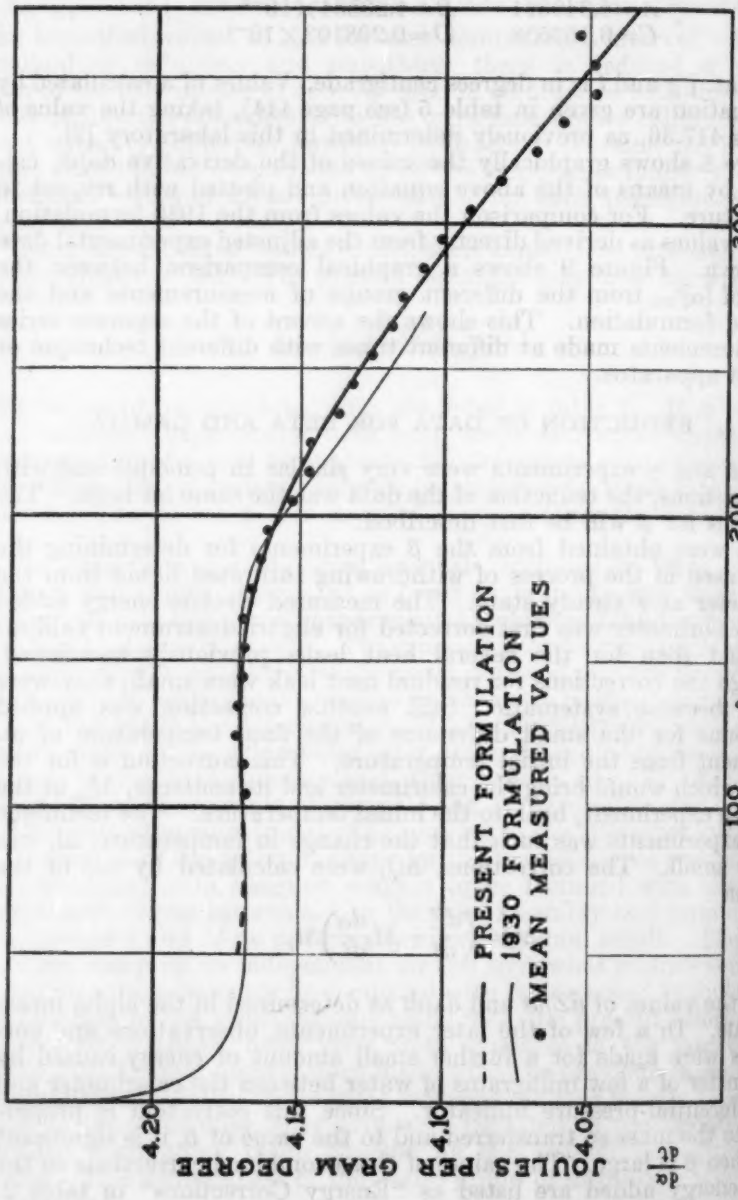

FIGURE 8.—*Graph of the alpha derivative, dα/dt.*

This correction was computed from the observed temperature of the withdrawn liquid and the specific heat at constant pressure. It varied with the temperature and with the rate of withdrawal of liquid. It

was about 1 j/g at 200° C but was as large as 10 j/g at one of the higher temperatures.

Another correction was needed to reduce the individual values of β to common temperatures so that they may be combined and compared. Since all the experiments were conducted very close to a chosen even temperature, the individual values were reduced to these even temperatures by interpolation, final adjustments being made as the formulation of the results progressed. These corrections described above are combined and listed in table 2 as "Corrections to Beta."

For the most part, the reduction of the data from the γ experiments was the same as in the above description for reduction of observations for β. The chief exception is that since no detectable superheat of the vapor was found in the γ experiments, this correction was not required. The data for the γ experiments and steps in the reduction are given in table 3.

Having calculated the values of β and γ for each of the accepted experiments, a study was made of their deviations from the averages

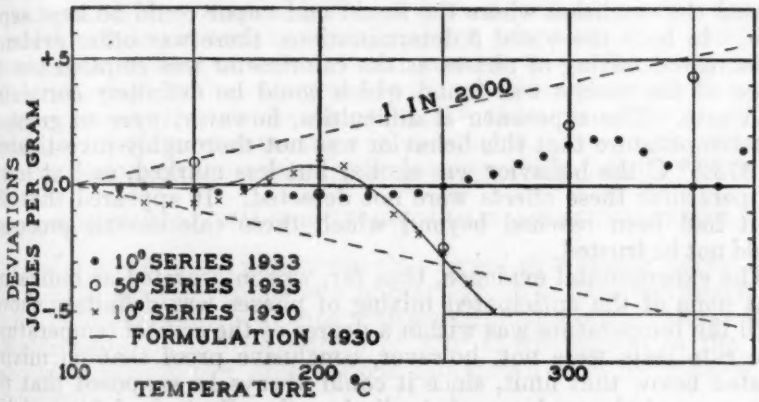

FIGURE 9.—*Deviation of $\alpha_t - \alpha_{100}$ from present formulation.*

for evidence of possible errors from mixing of phases and also to guide in weighting the results for the purpose of formulation.

One of the most commonly expressed causes for doubt of the reliability of data for heat of evaporation in the past has been the possibility of mixture of water drops in the steam. In the previous series of measurements in this laboratory, several measures had been taken to avoid this danger and to test its presence. Evaporation was then produced on the surface of a thin layer of water flowing over a heater of large area to promote quiet evaporation and thus avoid formation of any drops. Baffles were provided to intercept drops which might have been formed in spite of the first precaution. Finally, measurements were made at different rates of evaporation on the presumption that if drops were formed, the amount of liquid so entrained and carried out with the steam would vary with the rate and show a difference in the measured heat. No evidence of such an effect was found in the previous series of measurements extending from 50 to 270° C.

The present calorimeter was designed for higher working pressures and lacked a circulating pump. As a means of partially compensating for the lack of mechanical circulation, the evaporating process was

carried to the other extreme of actually inducing active boiling in the liquid. Baffles to intercept drops were, however, installed as before. The effect of mixing of phases was again looked for, even more carefully than before, and especially at the higher temperatures. It was reasoned that if there were mixing of phases, it would ordinarily be less, the lower the rate, and the results would consequently approach the normal value were it not for the lesser precision inherent in the lower rates. On the other hand, it seems certain that at some condition on approaching the critical state, the mixing of phases in these evaporation experiments would be unavoidable, regardless of the rate.

The experiments to investigate this effect were performed at widely different rates. In a number of cases at the higher temperatures, the rates ranged from 5 g/min down to less than 0.1 g/min. No definite indication of the effect was found in either the γ or β experiments even at temperatures up to and including 373° C.

At 374° C, however, the determinations of both γ and β were scattered much more widely than could be accounted for by inaccuracies of measurement. This scattering was attributed to having passed the condition where the liquid and vapor could be kept separate. In both the γ and β determinations, there was other evidence of increased mixing of phases as the calorimeter was emptied but no trend of the results was found which could be definitely correlated with rate. The experimental difficulties, however, were so great at this temperature that this behavior was not thoroughly investigated. At 373.5° C the behavior was similar but less marked, and at lower temperatures these effects were not detected. It appeared that the limit had been reached beyond which these calorimetric processes could not be trusted.

The experimental evidence, thus far, was interpreted as indicating that none of the anticipated mixing of phases was definitely shown until the temperature was within a degree of the critical temperature. The rate tests were not, however, conclusive proof that no mixing existed below that limit, since it could always be supposed that the rate was not changed enough to disclose the effect of mixing. Additional evidence by some entirely independent method would be more convincing, especially if obtained in the region well up toward the critical, for example, at 370° C or higher.

The desirability for such an additional check was further realized when the values of γ measured calorimetrically in this laboratory were compared with the values of specific volume of saturated vapor obtained by our colleagues in the steam research at the Massachusetts Institute of Technology, Messrs. Keyes, Smith, and Gerry [9]. Now that the vapor-pressure derivative is known with considerable accuracy, such comparisons are possible through the thermodynamic relations

$$\gamma = T u' \, dp/dt$$
$$\beta = T u \, dp/dt$$

These comparisons, made as the two investigations progressed, indicated a satisfactory accord in the lower range of temperature but showed a progressively increasing discord in the upper range. These discrepancies were too large to be accounted for by experimental error in either laboratory. Since the deviation was in the direction which would be caused by wet steam in the calorimetric experiments,

these were placed under suspicion. On the other hand, the saturation values obtained by the MIT group were the result of extrapolations from measurements made on superheated vapor, and not on vapor actually in the saturated condition. A considerable gap between the saturation limit and the actual measurements was left to be bridged in this manner. It was appreciated that these extrapolations were less reliable the greater the interval to be covered, and the nearer the critical region was approached. Additional specific-volume measurements made closer to the saturation limit, would be evidence which might decide whether or not there was actually a defect in the calorimetric data on account of wet steam which the special tests had failed to disclose.

Such measurements were therefore undertaken, using the calorimeter as a volume-measuring instrument. The feasibility of using the calorimeter for specific-volume measurements depended upon the accuracy with which the volumetric capacity of the calorimeter at a chosen temperature and pressure could be determined. It may be recalled that this instrument was designed primarily for calorimetric measurements, but that it had also proved well suited for vapor-pressure measurements, nevertheless, by adoption of a suitable experimental technique, it was found possible to use this instrument with all the precision necessary to test the reliability of the calorimetric measurements. It was decided to make the volumetric measurements at a selected temperature in the region where doubt existed but not so close to the critical state as to preclude definite results.

3. CONFIRMATORY SPECIFIC-VOLUME MEASUREMENTS

The purpose of these measurements was not to establish the saturation limit of specific volume as a primary group of data but merely to secure additional evidence concerning the reliability of the calorimetric measurements. The temperature of 370° C was chosen as the test point after preliminary observations had shown it to be suitable for the purpose.

The measurements of the mass of the sample, its temperature, and its pressure were made in the same manner as in the calorimetric experiments. By use of the differential-pressure indicator, a series of determinations was made at one chosen pressure and at several temperatures in the vicinity of the saturated state. Measurements were made as close to the saturation limit as would allow the state of the sample to be definitely known. Other measurements were taken a little further away from the saturation limit in order to guide the extrapolation over the small interval to the limit. In using the differential-pressure indicator, the pressure in the air reservoir was first balanced against the chosen saturation pressure in the calorimeter and then used as a reference pressure for successive measurements made in either the superheated-vapor or compressed-liquid region at this pressure.

The capacity of the calorimeter at 370° C was determined by several calibration experiments. The use of the calorimeter as a volume-measuring instrument was complicated by the fact that it had a tube at the bottom, which extended beyond the thermally controlled envelope space out to a valve and pressure cell which were near the temperature of the room. This tube contained a small mass of liquid

which must be accounted for as a tare to be deducted from the gross fluid contents of the system. However, this tare mass was nearly constant even when the calorimeter temperature was raised up to 370° C. This was so because the emergent column of liquid remained at the room temperature, except for a short length between the tube heater and the water cooling cell just below it. The entire temperature gradient from room temperature up to the calorimeter temperature came in this section of tube, which was only 25 mm long and 1.7 mm in diameter (volume 0.057 cm^3). The temperature of all the calorimeter system above this gradient section could be controlled as in the calorimetric measurements, and hence could be filled with vapor while the tare mass of liquid filled the part below. The position of the boundary meniscus was very definite because it had to be where the saturation temperature comes in the region of large temperature gradient. The tare mass was determined with the net capacity filled with superheated vapor at 110° C at 1 atmosphere pressure. After deducting about 0.19 g for this vapor, the tare mass was found to be 1.33 g. This tare value was probably reliable within 0.01 g, regardless of the different mean density in the gradient portion when used at 370° C. This uncertainty was one of the least important of several.

The net capacity was determined at 300 and 340° C with the system filled with liquid at about 217 atmospheres pressure. At these temperatures the specific volume of the compressed liquid has been determined by Smith and Keyes [8], and their data have been taken as reference values for this calibration. The thermal expansivity of the material of the calorimeter shell was known from determinations made at this Bureau so that the capacity at 370° C could be calculated, giving, after a small additional correction for elasticity, the capacity at 207.77 atmospheres, corresponding to saturation pressure at 370° C.

The determinations at 300 and 340° C, thus corrected, gave values of 330.56 and 330.65 cm^3, respectively, and a mean value of 330.6 cm^3. A third measurement of capacity was made with the calorimeter filled with liquid at 42.2° C under 1 atmosphere pressure. The specific volume of water is more accurately known here, but the correction for temperature and pressure to reduce to 370° C was much larger, hence only small weight could be given to this experiment as a calibration. The reduced value of 330.97 cm^3, which differed by about 1 part in 900 from the other measurements, was taken merely as a corroborative check.

The specific-volume measurements themselves were all made within 0.2° of 370° C. Seven measurements of the superheated vapor and six of the compressed liquid were made. In the vapor-volume experiments the reference air pressure in the pressure indicator was first balanced against the vapor pressure in the calorimeter at 370° C, with the calorimeter partly full of liquid. Next, the amount of fluid in the calorimeter was adjusted until, when allowed to reach a steady state with the reference pressure balanced, all parts of the calorimeter were slightly above the saturation temperature, as shown by readings of the thermoelements. This limiting condition was reached by making successive trials. When reached, it meant that the net capacity was filled with slightly superheated vapor, while the lower tube contained the tare mass of liquid.

The mean temperature of the calorimeter was then observed and the mass of fluid was determined in the usual way. This gave the

necessary data for determining a specific volume. Further withdrawal of a small amount of fluid and readjustment to a steady state at a slightly higher temperature gave data for another determination of the specific volume a little further out in the superheat.

Under the conditions of these experiments near 370° C, a gradient of two or three hundredths of a degree persisted in the calorimeter even after it reached a steady state. On this account, one determination made at a mean temperature only 0.01° C above saturation was distrusted because part of the net capacity was shown to be down to saturation temperature. The determination closest to saturation which could be trusted was at a mean temperature of about 0.03° C above saturation. Even at this point, there might have been question as to whether some of the inner surfaces of the calorimeter may not have still been wet on account of thermal lag. It might also be conceivable that liquid water could have been held in tiny capillary crevices, even though they were above the saturation temperature. Such a condition would of course give an erroneous result similar to the effect of wet steam in the calorimetric experiments on γ. To remove this uncertainty, a special test was made after one of the specific-volume determinations near 0.03° C superheat.

For this test the calorimeter was heated to about 2° C above the saturation temperature and allowed to remain an hour before cooling down again to the steady state at the reference pressure. The object of this heating was to evaporate any residual liquid and leave the surfaces dry. The calorimeter was then cooled by loss of heat from the outside, never allowing any part to go below the saturation temperature. If water had been evaporated by this process, the final temperature after cooling back to the original pressure should have been lower than before. Actually, no such change was found and it was therefore concluded that the determination could be trusted.

Five determinations were made between 0.03 and 0.06° C superheat and a sixth at about 0.16° C to give the trend of the isobar in this region.

The procedure for determining the specific volume of the compressed liquid was analogous to that for the superheated vapor except that the first measurements were made farthest from saturation. These measurements were made at temperatures between 0.16 and 0.17° C below the saturation temperature. The pressures were balanced against the pressure in the air reservoir kept over from the previous day's saturation balance. Some liquid was then withdrawn and two measurements made at about 0.05° C below saturation temperature. Further withdrawal brought the sixth measurement within 0.01° C of the saturation temperature. After this measurement, considerable water was withdrawn to establish saturation conditions again in the calorimeter to check the balancing air pressure in the air reservoir.

Very small departures from the intended constant pressure were observed in all the specific volume measurements. At the most, these corresponded to only 0.025 atmosphere on saturation pressure, or only 0.01° on saturation temperature. Where appreciable, corrections were applied to reduce the measurements to the pressure of 207.77 atmospheres corresponding to saturation at 370° C. The results of the specific volume measurements, thus reduced to this isobar, are given in table 4.

TABLE 4.—*Value of specific volume along 207.77 atmospheres (370° C sat.) isobar*

Temperature	Specific volume of liquid	Temperature	Specific volume of vapor
°C	cm³/g	°C	cm³/g
369.832	2.195	370.058	4.971
.836	2.195	.032	4.950
.835	2.195	.037	4.951
.950	2.213	.042	4.954
.956	2.213	.011	* 4.928
.994	* 2.230	.032	4.947
		.160	5.037

* Experiments under suspicion because of closeness to saturation.

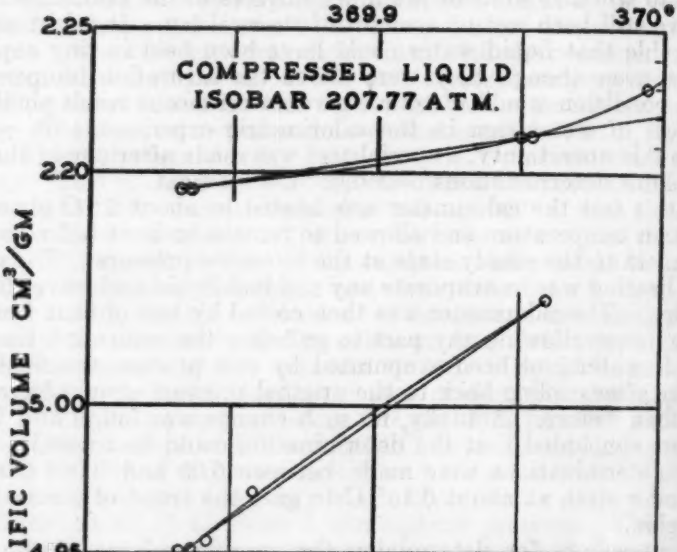

FIGURE 10.—*Graphs of volumetric measurements.*

The values from the experiments designated as suspicious may not have been erroneous but are perhaps not to be so fully trusted as the others because of the possibility that both phases may have been present in the volumetric space.

These results of the volumetric check measurements may now be examined for evidence bearing on the reliability of the calorimetric measurements, particularly in regard to the question as to whether or not the phases had been separated or partly mixed. Two graphs on figure 10 show how the observed isobaric volumes may be extrapolated to obtain values of specific volume at the 370° saturation limit. In each case, two suggested lines have been drawn, one a straight line,

disregarding the dubious near-saturation point, and the other line curved to include it. The increasing curvature in the latter case is in the sense expected from the known trend further away from the saturation limit, but it is also in the sense which would result from presence of both phases in the volumetric space.

In the case of the liquid, since the dubious point was approached from higher pressure it seems probable that no vapor space would have been formed even though the temperature at some point in the calorimeter may have been slightly above the saturation temperature. With this in mind, it seems fair to estimate the position of the experimental isobar at the saturation limit of 370° C as midway between the two drawn, thus giving a value of 2.227 cm^3/g for the specific volume of saturated liquid. A tolerance of 0.01 cm^3/g would seem to be adequate to cover both experimental error and uncertainty of this extrapolation. The mean value of β as derived from the reduced calorimetric observations is 359.4 int. j/g, while the adjusted value obtained from the formulation to be described later was 360.4 int. j/g. The specific volumes calculated from these values of β by the Clapeyron factor, Tdp/dt, are 2.220 and 2.226 cm^3/g, respectively. The agreement between the two methods is within the above tolerance and, consequently, the calorimetric result is corroborated by the volumetric.

Now returning to the graph of the volumetric data for the vapor, there is perhaps greater likelihood that the value closest to saturation was too low on account of condensed liquid because parts of the container were below the saturation temperature. With this in mind, the value of 4.925 cm^3/g has been estimated from the volumetric data as the specific volume of saturated vapor at 370° C. The mean observed value for γ is 800.4 int. j/g, while the adjusted value obtained from the formulation to be described later is 798.7 int. j/g. The specific volumes calculated from these values of γ by the Clapeyron factor, Tdp/dt, are 4.944 cm^3/g and 4.933 cm^3/g, respectively.

The mean observed calorimetric value is 0.019 cm^3/g higher than the preferred volumetric value. The formulated calorimetric value is 0.008 higher than the preferred volumetric value. These deviations are within a reasonable allowance for experimental errors. Moreover, the difference is in the opposite sense to the effect which would be caused by water mixed with the steam in the calorimetric measurements.

This experimental corroboration of both the γ and β measurements by independent volumetric measurements confirms the previous conclusion that these calorimetric results at 370° C show no decisive evidence of error attributable to mixture of phases, and that the increased spread of the results is the natural consequence of other inherent accidental errors.

This verification would perhaps be still more satisfactory if the deviations between the NBS and the MIT saturation values could be plausibly accounted for. Keyes, Smith, and Gerry, in their report [9] offer an explanation which, on examination, leads to a credible explanation and interpretation of these differences. On page 339 they suggest that their extrapolation may not be reliable, especially on approach to the critical region, and they give preference to other values for specific volume of saturated vapor in the temperature range above 350° C. The further examination of this matter can be

better made following the formulation of the calorimetric data, and it will therefore be resumed further on, where the formulated calorimetric data are available for comparison.

4. FORMULATION OF BETA AND GAMMA

From the study of the deviations of the individual values of β and γ from the averages, it was concluded to assign weights to these values in taking means at the even temperatures in preference to simple averages. For these means, weights were chosen proportional to the rate of withdrawal up to 2 g/min, above which rate the weight was taken as constant. This simple rule was in accord with judgment based on the physical facts and with estimates using the theory of probability. The mean values of β and γ at each even temperature are given in tables 2 and 3.

Deviations from these means were then used in estimating the weights to be assigned to the mean values in the formulation of the entire series with respect to temperature. Above 350° C, the assigned weights diminished rapidly with increasing temperature until at 374° C they were nearly zero. This is of course, the result of the behavior of the fluid and the limitation of the method on approach to the critical region. In other words, it means that even though the confirmatory tests at 370° C may have shown no gross errors to exist, there still is increasing uncertainty about determining the course of the saturation limit as the critical region is more closely approached.

In addition to the values of β and γ derived from this present series of measurements, there were other data available from measurements made with a previous calorimeter and published in 1930. These data include measurements of γ and β in the temperature range from 100 to 270° C, thus overlapping the range of the present determinations by 170° C. There were also the measurements of specific volume of liquid water by Smith and Keyes from which values of β could be calculated independently by use of the vapor pressure derivative, dP/dt. Values of β thus derived were used in the formulation in the range from 100 to 330° C. The values of β from calorimetric measurements in this range were in accord with those calculated from the volume data, but were less precise, and since the latter were from already smoothed and formulated data, they were the preferred choice. Above 330° C, the values of β from the calorimetric measurements were used since in this region there was an appreciable systematic difference from the volumetric values. A discussion of this choice of data on the saturated liquid may be found in the later section of this paper devoted to compilation of properties of saturated steam (page 424).

Having combined all the selected experimental values of γ and β to give single weighted mean values at certain even temperatures, empirical equations were deduced to represent smoothed and adjusted values. After considerable study of the fitting of the experimental values of γ and β to empirical equations, simultaneous equations for the sum and difference of these values were used in the formulation. From the theory, we have the relation $L=\gamma-\beta$, where L is the latent heat of vaporization and is one of the thermodynamic properties of steam sought. If we let $2D=\gamma+\beta$, D is the mean of γ and β, and in plane coordinates is the mean diameter of the figure formed by plotting γ and β against temperature. This mean diameter has less

curvature than γ or β and offers a means of extrapolation to a value at the critical temperature that is less speculative than the extrapolation of γ and β alone.

An equation for L was fitted to the weighted experimental mean values of γ and β in the range from 100 to 374.15° C. Another equation for D was fitted in the range from 330 to 374.15° C. The equation for D has the form

$$D=A+Bx^{0.617},$$

where $A=535.08$; $B=18.413$; $x=374.15-t$; and t is temperature in degrees centigrade. D is in int. j/g.

The equation for L has the form

$$L=a\left(\frac{374.15-t}{100}\right)^{0.404}-b\left(\frac{310-t}{100}\right)^{1.73}+c\left(\frac{165-t}{100}\right)^{2.2},$$

where $a=1585.19$; $b=36.75304$; $c=17.9218$; L is in int. j/g; t is in degrees centigrade; and $L=\gamma-\beta$.

The form of this equation has been chosen to conform with the accepted conventional interpretation that the latent heat approaches a zero value at the critical temperature at an infinite rate. As a result of this consideration, the temperature which is approached as a limit for real values of L is the numerical constant, 374.15, in the first term. This constant was determined to be the value which seemed to give the best fit with all the weighted experimental data. Although this evaluation of the critical temperature may not be decisive, yet it is an estimate which may be considered along with other recent published values.

Resuming the account of the formulation, after calculating from the equation for L, values in the range 100 to 374° C, and also values of D in the ranges 330 to 374° C, values of both γ and β could be found in the latter range by solution of the simultaneous equations. In the range from 100 to 330° C where the values of β calculated from specific-volume data of MIT had been adopted, values of γ were obtained by adding values of β to the corresponding values of L. The values of L, D, β, γ, and α, as finally deduced from the formulation of the experimental data, are given in table 5. The value of D yielded by the formula at the temperature of 374.15° C is the identical value of γ and β at this point where $L=0$.

VI. COMPILATION OF PROPERTIES OF SATURATED STEAM

Under this head the adjusted experimental data are assembled, combined, and tabulated in terms of the specific properties usually compiled in steam tables. Along with the description of this compilation, certain groups of similar data from other research laboratories have been examined, using graphs to exhibit the degree of accord. In this examination the aim has been to note considerations which apply to relative appraisals, rather than to attempt a general appraisal. In most cases, where differences were found, it has been possible to reconcile them as the result of interpretation of measurements, rather than to attribute them to experimental errors.

It has been shown above how adjusted and smoothed values of the calorimetric data have been deduced through use of empirical formulas. These computed values of α, β, and γ, as given in table 5, define the behavior of steam as far as the calorimetric survey goes. From them, corresponding values of enthalpy and entropy may be derived. By use of the vapor-pressure derivative, specific volumes also may be derived. Values of the factor $T\,dp/dT$ have been given in table 5, using the derivative dp/dT from Osborne and Meyers' [10] compilation.

Enthalpy of saturated liquid is derived from α and β according to the relation

$$H_t - H_0 = \alpha_t - \alpha_0 + \beta_t - \beta_0$$

The value of β_0 is 0.012 int. j/g.

Enthalpy of saturated vapor is derived from α and γ according to the relation

$$H'_t - H_0 = \alpha_t - \alpha_0 + \gamma_t - \beta_0$$

Entropy, ϕ, of saturated liquid is derived according to the relation

$$\phi\Big]_0^T = \int_0^T \frac{d\alpha}{T dT} dT + \frac{\beta}{T}\Big]_0^T$$

This formula may also be written

$$\phi\Big]_0^T = \frac{H}{T}\Big]_0^T + \int_0^T \frac{\alpha}{T^2} dT$$

As a check, the numerical calculations have been made by means of both forms.

The value of the entropy of saturated liquid at 100° C, 0.3120 IT cal [4] per gram degree, has been recalculated from the data in the report published in 1930 [2], using 273.16 as the absolute temperature of the ice point instead of 273.11, which value was used in that report.

Entropy, ϕ', of saturated vapor is derived according to the relation

$$\phi' = \phi + L/T$$

Calculated values of entropy, specific volume, enthalpy, latent heat, and vapor pressure, expressed in the units used in the International Steam Table are given in table 6.

The numerical values for properties of steam given in tables 5 and 6 represent the appraisal and formulation of the calorimetric measurements now completed in the range above 100° C. They supersede previous compilations which have been published from time to time as progress of the work advanced.

The adjusted and smoothed values of the properties of saturated steam having now been deduced from the experimental data, it will be convenient to resume examination of similar data from other sources. The first examination to be so made is the comparison of the MIT values for specific volume of saturated vapor.

[4] The International Steam Table calorie, denoted by the symbol IT cal, is defined as 1/860 international watthour which is equivalent to 4.18605 international joules. The report of the Third International Steam Table Conference held in America in September 1934, is given in Mechanical Engineering for November 1935.

This comparison is made on the basis of gamma ($T\,u'\,dp/dt$), since the values of this property are deducible from the MIT data for volume and vapor pressure, and are better proportioned for graphical comparison than are the specific volumes directly. The values of dp/dt from the MIT report on vapor pressure [11] were used for this conversion, since these have been preferred by the MIT group for the similar calculation of latent heat by the Clapeyron equation. Values of gamma thus obtained from the calculated values in table VI (MIT) [9] compared to the formulated values of gamma from table 5 of this paper are shown in figure 11, plotted with reference to temperature. From table 5 (MIT), deviations of the graphically extrapolated saturation volumes from the smoothed values given by equation 10 (MIT), may be similarly converted to deviations of gamma by use of the

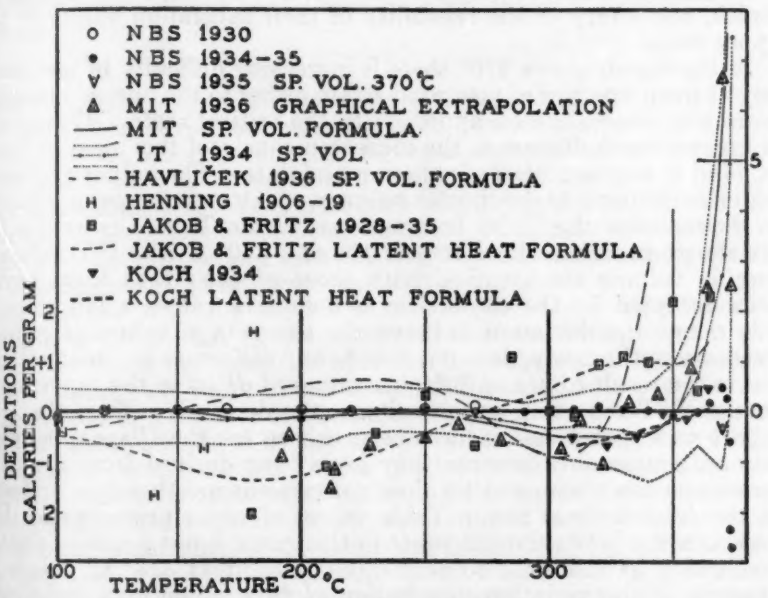

FIGURE 11.—*Comparison graph for saturated vapor.*

Clapeyron factor, $T\,dp/dt$. These deviations of the MIT extrapolated values from their smoothed values have also been plotted.

Inspection of the graph shows that in addition to the irregularities attributable to accidental errors of measurement, there appears to be a tendency to systematic departure of the MIT empirical formula 10 from the graphical extrapolation. Keyes, Smith, and Gerry have observed these deviations and have discussed the difficulty of graphical extrapolation, giving preference to saturation values deduced through their general formulation by an equation of state. A reason for the systematic tendency of the graphic extrapolation to low values at the lower temperatures is found in their statement that the effect of adsorption on the walls of the container tends to its largest effect near saturation and at the lower temperatures. They say elsewhere that "to give reliable saturation volumes, the analytical method using smoothing functions requires isometric pressures and temperatures

close to saturation." To reconcile these apparently conflicting views it may be inferred that an intrinsic characteristic of the equation of state has obviated the latter requirement at the lower temperatures.

It is interesting to note that, in the range of temperature from 100 to 250° C, the MIT formulation is in much better accord with the NBS calorimetric values than with the volumetric measurements nearest to saturation. It may be that the closeness of this accord is partly accidental, and it would therefore be a mistake to assume that it is a measure of the experimental accuracy.

From 250 to 350° C the accord of the two independent formulations is not so good but is perhaps within a reasonable allowance for experimental error.

Above 350°, and especially at 370°, the experimental evidence given previously in this paper confirms the doubt expressed by Keyes, Smith, and Gerry of the reliability of their saturation values in this upper range.

In the region above 370° there is increasing difficulty in measuring any of the properties of saturated steam owing to the phases becoming more and more alike on approach to the critical state. This results in greater indefiniteness in the measurements, and this must be borne in mind in any appraisal of experimental data. The values of gamma which correspond to the specific volumes of saturated vapor as adopted in the report of the Third International Steam Table Conference [12] are shown in figure 11. Between 100 and 360° C, the IST values of specific volume are identical with those of the MIT, these having been accepted by the conference as definitive values. Therefore, in this range, the deviation between the two sets of values of gamma, as shown in the figure, does not denote any difference in vapor volume, but is the result of use of different values of dP/dt in the conversions. In the MIT report on vapor volume, the derivatives from the MIT report on vapor pressure have been chosen for the Clapeyron calculations, presumably because they have been derived from the MIT measurements alone, and for their conversions are therefore preferred to the International Steam Table values of vapor pressure and their derivatives. While the difference in this range is not a serious matter, amounting at the most to only 0.057 percent at 315° C, this is an example of the variation in selection of data which may make comparisons appear either more or less in accord.

Another example illustrating this point is found in the present paper, where in the choice of values of specific volume of saturated liquid water from 100 to 330° C to use in formulating, those of the MIT have been chosen in preference to the values from the NBS calorimetric measurements of beta. Although the latter measurements were in satisfactory agreement, it was recognized that the formulated MIT values were more precise in most of this range. The reason for restricting the choice to this range is explained further on, where limitation of the extrapolation is discussed (page 427).

Another group of saturation data is the series of latent-heat measurements made at the Reichsanstalt. This work was started by Henning over 30 years ago and has been since continued by Jakob and Fritz. The measurements have extended over the temperature range from 30 to 365° C and have involved several modifications of the original apparatus.

The assembled results of this extensive research are given by Jakob and Fritz [13] in their recent report. In this report an empirical formula for latent heat of vaporization is given and also values calculated therefrom, extending from 0 to 372° C. Corresponding values of specific volume of saturated vapor, computed by use of the Clapeyron equation, are also given. These experimenters used a method in which the measured quantity, called by them "specifischer Wärmeaufwand", is the same as the gamma of the present paper. This quantity will therefore be taken as the basis of comparisons in preference to the values of latent heat which have been deduced from the experimental data by use of a correction which corresponds to the beta of this paper. The values of beta used by Jakob and Fritz were calculated from the Smith and Keyes data for specific volume of saturated liquid water, using the vapor-pressure derivative from the vapor-pressure tables of Osborne and Meyers. The values of gamma corresponding to the smoothed values of latent heat have been calculated by restoring these values of beta according to the relation

$$\gamma = L + \beta$$

These smoothed values of gamma from the Reichsanstalt data have been plotted as deviations from the NBS gamma taken as reference. Deviations of the experimental or measured values as given by Jakob and Fritz in their table 8 have also been plotted.

By inspection of this graph, an idea may be gained of the relative accord of the different independent series of calorimetric measurements with each other and with the respective formulations by which the experimental data are smoothed and interpreted.

The method of these experimenters employed the same general principle as that used at the National Bureau of Standards. In both laboratories, the water is evaporated in a calorimeter by measured electric heating, the vapor withdrawn from the calorimeter, condensed, and collected in a receiver for determination of the mass. There are, however, several features of the details of the apparatus, and of the technique of manipulation, which distinctly differentiate the two methods.' Aside from the relative size and the degree of thermal insulation of calorimeters from envelopes, one other marked difference is the means of handling the withdrawn vapor and bringing it down from the saturation state in the calorimeter to the state in the receiver. The National Bureau of Standards technique was to throttle the vapor through a sensitive adjusting valve down to the low pressure before leading outside into a detachable receiver where it was condensed and weighed. The Reichsanstalt technique was to collect the condensate in a receiver where the total pressure was kept nearly equal to the pressure in the calorimeter by an artificial atmosphere of gas. In this scheme the pressure of the steam is reduced by diffusion through the gas to the condensation pressure. From the receiver it was transferred to a weighing vessel at atmospheric pressure. There were also considerable differences in the manner of observing temperatures and temperature distribution. It is not possible to estimate how these and other differences in technique may have affected the results.

It will be recalled that in the two regions where the deviation between the results of the two laboratories is most appreciable, the

NBS results have been doubly established. In the lower range from 100 to 270° C, this verification was by repetition of the measurements in an entirely different calorimeter, while at 370° C the determinations by calorimetric measurement were corroborated by volumetric measurements. The differences which remain between the final smoothed formulations of the results may perhaps be taken as evidence of the inherent difficulty of this type of physical measurement.

The latent heat in the pressure range from 100 to 200 kg/cm² (310 to 365° C) has been determined by We. Koch [14] at the Technische Hochschule München, using an entirely different method of calorimetry than either the NBS or the PTR. An electrically heated flow calorimeter was used. Compressed liquid water at a determined temperature and pressure entered the calorimeter, where on receiving the energy supplied by a measured electric-power input, the water was heated, evaporated, and the vapor superheated to a state determined by the observed temperature and pressure. Experimental data obtained from separate measurements on the heat capacity of compressed liquid water and on superheated vapor, when extrapolated to the saturation limit, furnished the corrections by which the latent heat could be deduced from the evaporation measurements. The water rate was determined by weighing the water condensed during a determined time while a steady rate was kept. The formula for latent heat given by Koch is similar in type to those given by Jakob and Fritz, and to the one given in this paper, but fewer terms are required in Koch's formula because of the lesser interval covered.

The smoothed values calculated by Koch [4] have been plotted in figure 11 as deviations from the NBS formula for latent heat, assuming that these deviations are the same for gamma as for latent heat, or that beta is the same for both. Koch's determinations of latent heat are subject to any uncertainty which there may be in the extrapolations to the saturation limit, in addition to any experimental errors of measurement. Nevertheless, the degree of accord of this determination by a dissimilar calorimetric method is noteworthy, particularly toward the higher temperatures, where it is in contrast to the deviations of the Jakob and Fritz values.

Still another evaluation of values of properties of saturated steam is found in the recent publication of Havlíček and Mĺskovský [15]. These authors present the results of an extensive research conducted at the Witkowitz Collieries in Moravska Ostrava, Czechoslovakia. They have measured the enthalpy of superheated steam in the range of pressures from 1 to 400 kg/cm² and in the range of temperatures from 20 to 550° C. The experimental method used a condensing calorimeter by which the heat given out by steam, initially at a determined temperature and pressure, is absorbed by cooling water and thus measured. A large number of points were thus established in the enthalpy field of superheat, including one isobar very near the critical pressure.

The experimental results of this calorimetric survey have been formulated by Juza [15], a coworker, in a supplementary contribution, using an equation of state somewhat analogous to that of the MIT. There is, however, this distinct difference in that, while the MIT group deduce enthalpies from their volumetric measurements,

[4] An error in calculation at 245° has been corrected. The value is 229.9 instead of 230.4 cal/g.

Juza deduces specific volumes from the calorimetric measurements of enthalpy obtained by Havliček and his associates.

From this formulation, when supplemented by vapor-pressure data, there is deduced a series of values of specific volume and enthalpy of saturated vapor, which may be compared with the results of the present paper. For this comparison, the specific volumes are reduced to the corresponding values of gamma, as in the comparison of the MIT results. These Havliček-Juza values of gamma are plotted in figure 11 as deviations from the NBS values.

It should be borne in mind, in any appraisal of saturation values of either specific volume, latent heat, or vapor enthalpy that the saturation values from the Havliček survey, and likewise those from the MIT measurements, as well as those of Koch, all depend on extrapolation of one kind or another from measurements at other than the saturation state. It should, therefore, be well considered whether these indirect evaluations and direct measurements upon the saturated fluid should be regarded as equally definitive. In this connection the completeness with which the path of approach to saturation is experimentally established may be fully as important a factor as accuracy of measurements.

As an extreme example of the uncertainty in extrapolating superheat data to the saturation limit, figure 12 shows two graphical extrapolations of a 225 kg/cm^2 isobar of enthalpy, along with the saturation limit of enthalpy from the NBS measurements. The superheat data were taken from Havliček's measurements. It is apparent that without experimental points nearer to saturation than the 3.9° in the compressed liquid or 6.1° in the superheat the location of the saturation limit by means of extrapolation, may be uncertain by from 20 to 40 calories. Many other less extreme cases may be found in study of the experimental data which are now available.

One of these which has a direct bearing on the choice of auxiliary data used in formulating the results of the NBS measurements, is illustrated graphically in figure 13. This graph exhibits the experimental data for specific volume of liquid water from the work of Smith and Keyes [8]. Not all their results are shown, but only those in the region where certain differences are found between their derived saturation values and those of the NBS. The portions near saturation of six of their isothermals are shown plotted against pressures. The observed points are shown, also the calculated saturation values, and the NBS saturation values. For the 320 and 330° C isothermals, smooth curves fit all the points well, including the NBS values.

For the 340, 350, and 360° isothermals, there is increasing discrepancy between the calculated saturation values and the trend indicated by the experimental points, which is confirmed by the NBS values. At 350° the entire course of the calculated isothermal differs systematically from the experimental.

The 370° isothermal approaches the saturation limit so gradually that it would be impossible to determine the saturation limit from the trend beyond the nearest experimental point, 5.75 atmospheres away.

From a consideration of these facts it was concluded that while no conflict was shown between the values deduced from the NBS beta measured calorimetrically, and the actual measurements of the MIT on compressed liquid water, the saturation values deduced by Smith and Keyes from the MIT measurements above 330° were open to

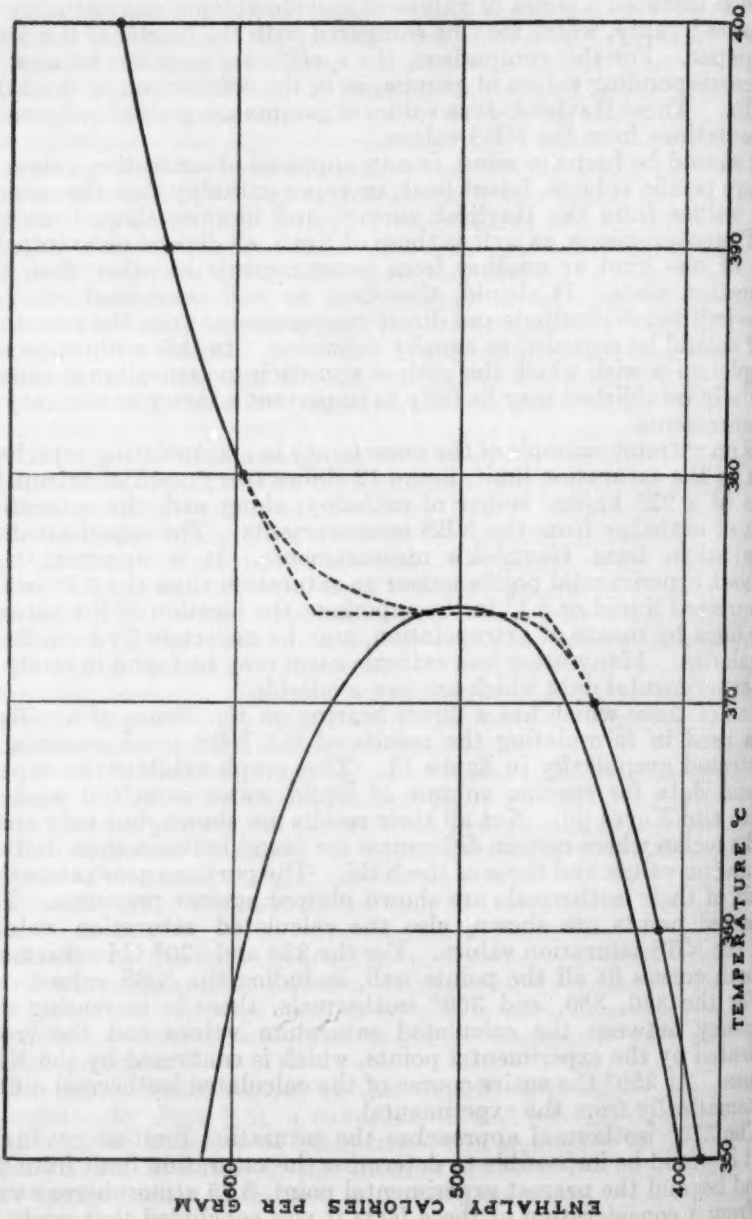

FIGURE 12.—*Example of uncertain extrapolation.*

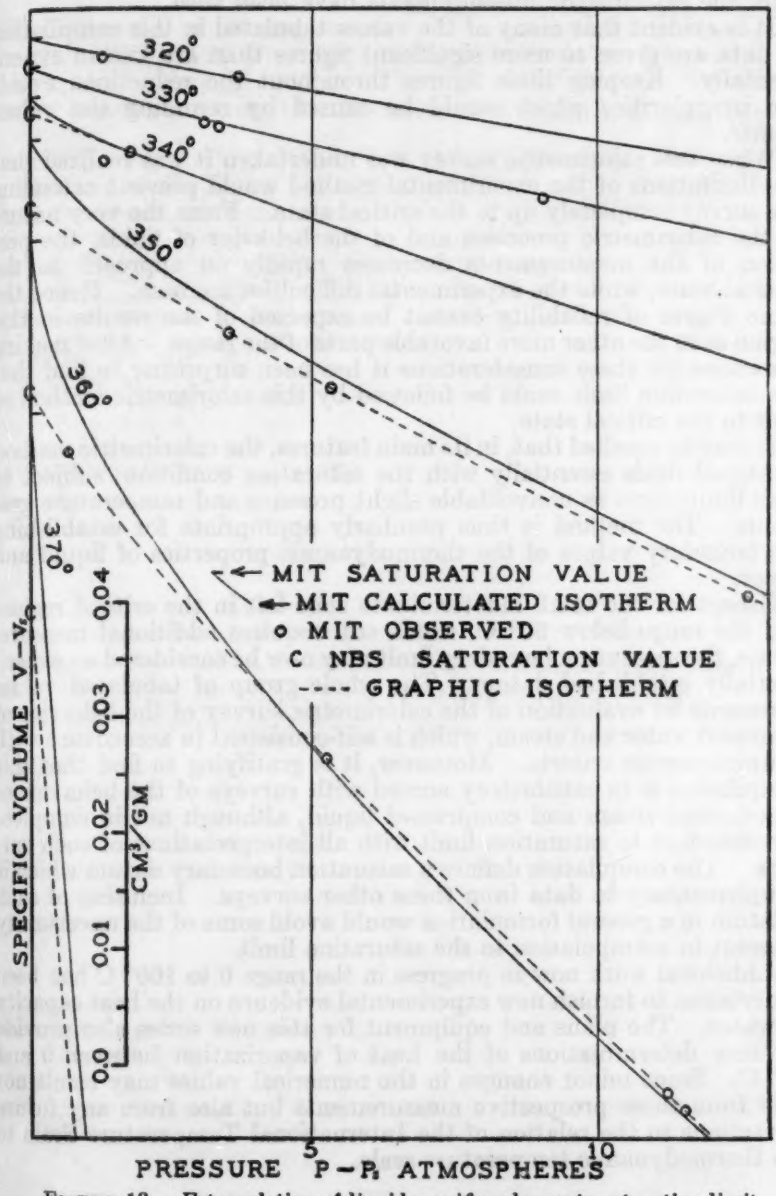

FIGURE 13.—*Extrapolation of liquid specific volumes to saturation limit.*

question. The NBS compilation has, therefore, accepted the values from the MIT formulation only up to and including the 330° point for the values of beta used, while above this point values formulated from the calorimetric measurements have been used.

It is evident that many of the values tabulated in this compilation of data are given to more significant figures than are known experimentally. Keeping these figures throughout the reductions avoids the irregularities which would be caused by rounding the values sooner.

When this calorimetric survey was undertaken it was realized that the limitations of the experimental method would prevent extending the survey completely up to the critical state. From the very nature of the calorimetric processes and of the behavior of fluids, the precision of the measurements decreases rapidly on approach to the critical state, while the experimental difficulties increase. Hence the same degree of reliability cannot be expected of the results in this region as in the other more favorable parts of the range. After making allowance for these considerations it has been surprising to find that the saturation limit could be followed by this calorimetric method so near to the critical state.

It may be recalled that, in its main features, the calorimetric method employed deals essentially with the saturation condition, subject to such limitations as unavoidable slight pressure and temperature gradients. The method is thus peculiarly appropriate for establishing the boundary values of the thermodynamic properties of liquid and vapor.

Except for the small indeterminate zone left in the critical region and the range below 50° C, which still requires additional measurements, the saturation boundary limit may now be considered an experimentally established datum. The whole group of tabulated values represents an evaluation of the calorimetric survey of the behavior of saturated water and steam, which is self-consistent in accordance with thermodynamic criteria. Moreover, it is gratifying to find that this compilation is in satisfactory accord with surveys of the behavior of superheated steam and compressed liquid, although not in complete agreement as to saturation limit with all interpretations of such surveys. The compilation defines a saturation boundary datum which is complementary to data from these other surveys. Inclusion of such a datum in a general formulation would avoid some of the uncertainty inherent in extrapolation to the saturation limit.

Additional work now in progress in the range 0 to 100° C has been undertaken to furnish new experimental evidence on the heat capacity of water. The plans and equipment for this new series also provide for new determinations of the heat of vaporization between 0 and 50° C. Some minor changes in the numerical values may result not only from these prospective measurements but also from any future corrections to the relation of the International Temperature Scale to the thermodynamic temperature scale.

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WASHINGTON, February 10, 1937.

VIII. TABLES OF DATA AND PROPERTIES OF STEAM

TABLE 1.—*Principal data from α experiments*

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Entire energy added Q	Energy for even temperature interval $Q]_{t_1}$	$\alpha]_{t_1}$	Deviation $\alpha]_{t_1}-\alpha_m$
	g	°C	°C	*Int.* j	*Int.* j	*Int.* j	*Int.* j/g	*Int.* j/g
6-6-33	248.316	100.024	110.122	−6.1	17,043.0	16,876.8	41.689	0.002
6-7-33	43.074	100.016	110.052	−0.1	8,351.6	8,320.6	41.691	.004
6-8-33	43.074	100.082	110.078	−.9	8,317.1	8,320.2	41.682	−.005
6-12-33	250.163	100.052	110.096	−.9	17,028.1	16,953.0	41.686	−.001
6-14-33	44.159	100.020	110.175	−.6	8,495.6	8,365.1	41.674	−.013
Even-temperature interval t_1 to t_2=100 to 110°. $Z]_{100}^{110}$=6,524.8 int. j. Mean value of $\alpha]_{100}^{110}$=41.687 int. j/g.								
6-5-33	248.316	109.993	119.900	−2.0	16,792.5	16,950.4	41.699	.002
6-6-33	248.316	110.122	120.132	−7.7	16,968.3	16,951.1	41.702	.005
6-7-33	43.074	110.052	120.198	−0.3	8,515.7	8,393.2	41.726	.029
6-8-33	43.074	110.078	119.987	−.5	8,314.3	8,390.6	41.666	−.031
6-12-33	250.163	110.096	119.976	−6.2	16,822.7	17,026.4	41.695	−.002
6-14-33	44.159	110.175	119.798	−0.6	8,117.4	8,436.1	41.672	−.025
Even-temperature interval t_1 to t_2=110 to 120°. $Z]_{110}^{120}$=6,595.9 int. j. Mean value of $\alpha]_{110}^{120}$=41.697 int. j/g.								
6-5-33	248.316	119.900	129.988	−.7	17,178.8	17,029.8	41.713	−.001
6-6-33	248.316	120.132	130.118	−6.0	17,005.8	17,028.6	41.708	−.006
6-7-33	43.074	120.198	130.058	0.7	8,353.5	8,471.1	41.772	.058
6-8-33	43.074	119.987	130.032	−.5	8,506.8	8,468.4	41.710	−.004
6-12-33	250.163	119.976	130.076	−6.1	17,277.3	17,107.3	41.715	.001
6-14-33	44.159	119.798	129.841	−0.5	8,548.4	8,513.5	41.706	−.008
Even-temperature interval t_1 to t_2=120 to 130°. $Z]_{120}^{130}$=6,671.8 int. j. Mean value of $\alpha]_{120}^{130}$=41.714 int. j/g.								
6-5-33	248.316	129.988	139.963	−.7	17,069.2	17,113.0	41.717	.002
6-6-33	248.316	130.118	140.055	−6.1	17,008.4	17,114.4	41.722	.007
6-7-33	43.074	130.058	140.088	−0.5	8,578.9	8,552.5	41.751	.036
6-8-33	43.074	130.032	140.109	−.8	8,617.8	8,551.3	41.724	.009
6-12-33	250.163	130.076	140.136	−6.7	17,294.2	17,188.4	41.710	−.005
6-14-33	44.159	129.841	140.181	−0.5	8,886.9	8,593.5	41.654	−.061
Even-temperature interval t_1 to t_2=130 to 140°. $Z]_{130}^{140}$=6,754.1 int. j. Mean value of $\alpha]_{130}^{140}$=41.715 int. j/g.								
6-5-33	248.316	139.963	150.216	−.6	17,637.1	17,199.4	41.698	.010
6-6-33	248.316	140.055	150.093	−7.5	17,263.3	17,198.3	41.691	.003
6-7-33	43.074	140.088	150.040	−0.6	8,601.2	8,641.8	41.698	.012
6-8-33	43.074	140.109	150.081	−.9	8,618.2	8,641.6	41.693	.007
6-12-33	250.163	140.136	150.123	−6.7	17,248.7	17,270.9	41.674	−.012
6-14-33	44.159	140.183	149.904	0.6	8,444.4	8,686.9	41.693	.009
Even-temperature interval t_1 to t_2=140 to 150°. $Z]_{140}^{150}$=6,845.7 int. j. Mean value of $\alpha]_{140}^{150}$=41.686 int. j/g.								
6-5-33	248.316	150.216	160.190	−.4	17,246.5	17,200.5	41.678	−.005
6-6-33	248.316	150.093	160.164	−6.6	17,420.8	17,296.0	41.700	.017
6-7-33	43.074	150.040	159.940	−0.2	8,649.0	8,736.6	41.682	−.001
6-8-33	43.074	150.081	159.946	−.6	8,619.5	8,737.4	41.700	.017
6-12-33	250.163	150.123	160.018	−6.9	17,181.3	17,363.9	41.664	−.019
6-14-33	44.159	149.904	159.796	−0.3	8,686.5	8,782.7	41.702	.019
Even-temperature interval t_1 to t_2=150 to 160°. $Z]_{150}^{160}$=6,941.2 int. j. Mean value of $\alpha]_{150}^{160}$=41.683 int. j/g								
6-5-33	248.316	160.190	170.082	.4	17,215.0	17,401.9	41.705	.012
6-6-33	248.316	160.164	170.164	−6.7	17,398.0	17,396.6	41.684	−.009
6-7-33	43.074	159.940	169.924	−0.5	8,527.9	8,843.7	41.740	.047
6-8-33	43.074	159.946	169.877	.3	8,779.5	8,841.3	41.684	−.009
6-12-33	250.163	160.018	169.937	−6.8	17,333.4	17,474.4	41.687	−.006
6-14-33	44.159	159.796	170.103	−0.6	9,158.2	8,885.7	41.665	−.028
Even-temperature interval t_1 to t_2=160 to 170°. $Z]_{160}^{170}$=7,045.8 int. j. Mean value of $\alpha]_{160}^{170}$=41.693 int. j/g.								

TABLE 1.—*Principal data from a experiments*—Continued

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Entire energy added Q	Energy for even temperature interval $Q]_{t_1}^{t_2}$	$\alpha]_{t_1}^{t_2}$	Deviation $\alpha]_{t_1}^{t_2}-\alpha_m$
	g	°C	°C	*Int.* j	*Int.* j	*Int.* j	*Int.* j/g	*Int.* j/g
6-5-33	248.316	170.082	179.968	−0.5	17,295.1	17,493.9	41.625	−0.010
6-6-33	248.316	170.164	180.066	−8.0	17,330.8	17,501.2	41.655	.020
6-7-33	43.074	169.924	179.906	−0.6	8,933.9	8,950.4	41.619	−.016
6-8-33	43.074	169.877	179.919	− .6	8,987.1	8,950.7	41.626	−.009
6-12-33	250.163	169.937	180.030	−8.1	17,735.5	17,572.1	41.630	−.005
6-14-33	44.159	170.103	180.021	−0.1	8,922.3	8,995.5	41.618	−.017

Even-temperature interval t_1 to t_2=170 to 180°. $Z]_{170}^{180}$=7,157.7 int. j. Mean value of $\alpha]_{170}^{180}$=41.635 int. j/g.

6-5-33	248.316	179.968	189.921	−1.4	17,530.0	17,613.0	41.622	.000
6-6-33	248.316	180.066	189.923	−8.6	17,362.6	17,615.3	41.632	.010
6-7-33	43.074	179.906	189.872	0.3	9,038.1	9,070.7	41.631	.009
6-8-33	43.074	179.919	190.011	.3	9,154.2	9,071.1	41.640	.018
6-12-33	250.163	180.030	189.993	−8.5	17,622.5	17,687.3	41.612	−.010
6-14-33	44.159	180.025	189.880	0.1	8,981.1	9,114.2	41.593	−.029

Even-temperature interval t_1 to t_2=180 to 190°. $Z]_{180}^{190}$=7,277.5 int. j. Mean value of $\alpha]_{180}^{190}$=41.622 int. j/g.

6-5-33	248.316	189.921	199.952	−1.0	17,788.7	17,734.8	41.594	.003
6-6-33	248.316	189.923	199.877	−9.3	17,654.3	17,736.1	41.600	.009
6-7-33	43.074	189.872	199.896	0.8	9,217.0	9,195.8	41.545	−.046
6-8-33	43.074	190.011	200.258	−1.1	9,427.6	9,198.2	41.601	.010
6-12-33	250.163	189.993	199.951	−9.2	17,731.5	17,807.2	41.576	−.015
6-14-33	44.159	189.880	199.914	0.2	9,275.9	9,245.4	41.647	.056

Even-temperature interval t_1 to t_2=190 to 200°. $Z]_{190}^{200}$=7,406.3 int. j. Mean value of $\alpha]_{190}^{200}$=41.591 int. j/g.

6-5-33	248.316	199.952	210.012	−1.3	17,968.1	17,860.6	41.547	.006
6-6-33	248.316	199.877	209.833	−10.0	17,781.9	17,862.3	41.554	.013
6-7-33	43.074	199.896	210.096	−1.6	9,524.6	9,338.1	41.659	.118
6-8-33	43.074	200.258	210.086	0.2	9,171.2	9,329.5	41.459	−.082
6-12-33	250.163	199.951	210.021	−10.8	18,057.8	17,932.8	41.529	−.012
6-14-33	44.159	199.914	210.163	−1.2	9,508.6	9,374.5	41.459	.018

Even-temperature interval t_1 to t_2=200 to 210°. $Z]_{200}^{210}$=7,543.7 int. j. Mean value of $\alpha]_{200}^{210}$=41.541 int. j/g.

6-5-33	248.316	210.012	220.067	−4.7	18,099.0	17,999.7	41.528	.017
6-6-33	248.316	209.833	219.858	−10.4	18,038.8	17,997.2	41.518	.007
6-7-33	43.074	210.084	220.221	−0.6	9,607.9	9,475.4	41.503	−.008
6-8-33	43.074	210.105	220.048	−1.1	9,421.9	9,473.9	41.468	−.043
6-12-33	250.163	210.021	220.072	−10.7	18,162.2	18,068.4	41.496	−.015

Even-temperature interval t_1 to t_2=210 to 220°. $Z]_{210}^{220}$=7,687.7 int. j. Mean value of $\alpha]_{210}^{220}$=41.511 int. j/g.

6-5-33	248.316	220.067	230.259	−15.8	18,496.2	18,146.0	41.484	.026
6-6-33	248.316	219.858	230.010	−13.0	18,421.7	18,145.1	41.481	.023
6-7-33	43.074	220.221	230.017	−1.2	9,430.8	9,625.6	41.343	−.115
6-8-33	43.074	220.048	229.964	−1.5	9,544.1	9,626.0	41.352	−.106
6-12-33	250.163	220.072	230.234	−13.0	18,509.4	18,212.4	41.443	−.015

Even-temperature interval t_1 to t_2=220 to 230°. $Z]_{220}^{230}$=7,844.8 int. j. Mean value of $\alpha]_{220}^{230}$=41.458 int. j/g.

6-5-33	248.316	230.259	240.228	−15.3	18,240.2	18,292.7	41.414	.014
6-6-33	248.316	230.010	240.177	−16.0	18,602.4	18,295.3	41.425	.025
6-7-33	43.074	230.017	239.947	−1.3	9,717.6	9,786.8	41.275	−.125
6-8-33	43.074	229.964	239.934	−2.0	9,758.6	9,788.5	41.315	−.085
6-12-33	250.163	230.234	240.105	−14.5	18,129.8	18,364.5	41.395	−.005

Even-temperature interval t_1 to t_2=230 to 240°. $Z]_{230}^{240}$=8,008.9 int. j. Mean value of $\alpha]_{230}^{240}$=41.400 int. j/g.

TABLE 1.—*Principal data from α experiments*—Continued

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Entire energy added Q	Energy for even temperature interval $Q]_{t_1}^{t_2}$	$\alpha]_{t_1}^{t_2}$	Deviation $\alpha]_{t_1}^{t_2}-\alpha_m$
	g	°C	°C	*Int.* j	*Int.* j	*Int.* j	*Int.* j/g	*Int.* j/g
6-5-33	248.316	240.228	250.012	−16.6	18,056.6	18,452.8	41.368	0.009
6-6-33	248.316	240.177	249.933	−15.9	18,004.3	18,455.2	41.378	.019
6-7-33	43.074	239.947	249.701	−1.6	9,713.3	9,961.3	41.343	−.016
6-8-33	43.074	239.934	250.058	−2.3	10,086.0	9,962.0	41.359	.000
6-12-33	250.163	240.105	250.042	−15.5	18,405.4	18,521.1	41.335	−.024
Even-temperature interval t_1 to t_2=240 to 250°. $Z]_{240}^{250}$=8,180.5 int. j. Mean value of $\alpha]_{240}^{250}$=41.359 int. j/g.								
5-26-33	219.812	249.968	259.557	−1.3	16,720.8	17,441.9	41.266	−.021
5-29-33	216.625	249.999	259.864	0.8	17,081.8	17,316.8	41.295	.008
5-31-33	67.996	250.029	260.236	.4	11,417.6	11,183.5	41.360	.073
6-1-33	175.636	249.999	260.234	−15.1	15,989.3	15,620.5	41.275	−.012
Even-temperature interval t_1 to t_2=250 to 260°. $Z]_{250}^{260}$=8,371.2 int. j. Mean value of $\alpha]_{250}^{260}$=41.287 int. j/g.								
5-26-33	219.812	259.557	269.884	−2.0	18,208.8	17,637.2	41.220	.005
5-29-33	216.625	259.864	270.060	−1.0	17,846.1	17,503.7	41.210	−.006
5-31-33	67.996	260.236	269.966	0.3	11,074.3	11,379.0	41.214	−.001
6-1-33	175.636	260.234	270.347	−2.3	15,999.6	15,815.8	41.217	.002
Even-temperature interval t_1 to t_2=260 to 270°. $Z]_{260}^{270}$=8,576.6 int. j. Mean value of $\alpha]_{260}^{270}$=41.215 int. j/g.								
5-26-33	219.812	269.884	280.005	−1.8	18,041.9	17,826.4	41.151	−.010
5-29-33	216.625	270.060	280.133	1.0	17,828.3	17,698.1	41.164	.003
5-31-33	67.996	269.966	279.983	−0.3	11,600.5	11,582.0	41.194	.033
6-1-33	175.636	270.347	280.128	−.1	15,664.6	16,009.5	41.156	−.005
Even-temperature interval t_1 to t_2=270 to 280°. $Z]_{270}^{280}$=8,781.0 int. j. Mean value of $\alpha]_{270}^{280}$=41.161 int. j/g.								
5-26-33	219.812	280.005	289.945	−1.7	17,935.0	18,043.8	41.101	.024
5-29-33	216.625	280.133	289.808	−1.5	17,318.8	17,902.3	41.053	−.024
6-1-33	175.636	280.128	290.147	−2.1	16,257.2	16,224.3	41.080	.003
Even-temperature interval t_1 to t_2=280 to 290°. $Z]_{280}^{290}$=9,009.2 int. j. Mean value of $\alpha]_{280}^{290}$=41.077 int. j/g.								
-26-33	219.812	289.945	299.750	0.4	17,910.2	18,270.5	40.998	−.014
5-29-33	216.625	289.808	299.976	−2.6	18,452.2	18,150.1	41.045	.033
5-31-33	67.996	289.885	299.985	1.1	12,163.2	12,044.9	40.976	−.036
5-1-33	175.636	290.147	300.251	−1.1	16,636.8	16,460.2	41.002	−.010
6								
Even-temperature interval t_1 to t_2=290 to 300°. $Z]_{290}^{300}$=9,258.7 int. j. Mean value of $\alpha]_{290}^{300}$=41.012 int. j/g.								
5-29-33	67.996	299.992	309.968	−3.1	12,279.8	12,310.2	40.927	.014
5-31-33	67.996	299.568	309.818	−1.6	12,605.3	12,306.2	40.869	−.044
6-1-33	175.636	300.251	310.234	−1.1	16,686.7	16,708.9	40.889	−.024
6-2-33	175.636	300.004	309.996	−1.6	16,693.6	16,707.0	40.878	−.035
7-21-33	161.675	299.871	310.103	−2.6	16,529.0	16,154.4	40.990	.077
Even-temperature interval t_1 to t_2=300 to 310°. $Z]_{300}^{310}$=9,527.3 int. j. Mean value of $\alpha]_{300}^{310}$=40.913 int. j/g.								
5-29-33	67.996	309.968	320.062	−2.5	12,721.1	12,601.0	40.791	−.018
5-31-33	67.996	309.818	319.844	−0.2	12,629.5	12,601.6	40.799	−.010
6-1-33	175.636	310.234	320.080	−.4	16,732.4	16,990.0	40.781	−.028
6-2-33	175.636	309.996	320.148	−1.8	17,253.9	16,992.5	40.795	−.014
7-21-33	161.675	310.103	319.971	1.0	16,218.0	16,434.6	40.867	.058
Even-temperature interval t_1 to t_2=310 to 320°. $Z]_{310}^{320}$=9,827.4 int. j. Mean value of $\alpha]_{310}^{320}$=40.809 int. j/g.								
5-29-33	67.996	320.062	330.275	−3.7	13,208.1	12,926.9	40.644	−.037
5-31-33	67.996	319.844	329.890	−0.4	12,982.6	12,928.2	40.663	−.018
6-1-33	175.636	320.080	329.930	.1	17,045.2	17,304.6	40.660	−.021
6-2-33	175.636	320.148	330.098	−.9	17,224.0	17,306.1	40.668	−.013
7-21-33	161.675	319.971	330.043	−2.2	16,872.5	16,750.5	40.743	.062
Even-temperature interval t_1 to t_2=320 to 330°. $Z]_{320}^{330}$=10,163.3 int. j. Mean value of $\alpha]_{320}^{330}$=40.681 int. j/g.								

TABLE 1.—*Principal data from a experiments*—Continued

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Entire energy added Q	Energy for even temperature interval Q_1[2]	$\alpha]_1$[3]	Deviation $\alpha]_1-\alpha_m$
	g	°C	°C	*Int.* j	*Int.* j	*Int.* j	*Int.* j/g	*Int.* j/g
5-29-33	67.996	330.275	340.149	−4.8	13,153.2	13,312.4	40.591	−0.001
5-31-33	67.996	329.890	340.306	0.3	13,871.9	13,313.1	40.601	.009
6-1-33	175.636	329.930	339.979	−.6	17,760.8	17,674.9	40.553	−.039
7-21-33	161.675	330.043	339.958	−1.6	16,976.6	17,121.8	40.633	.041
Even-temperature interval t_1 to t_2=330 to 340°. $Z]_{330}^{340}$=10,552.4 int. j. Mean value of $\alpha]_{330}^{340}$=40.592 int. j/g.								
5-29-33	67.996	340.149	350.051	−1.6	13,638.8	13,768.0	40.257	−.222
5-31-33	67.996	340.306	350.143	0.1	13,565.4	13,777.2	40.392	−.087
6-1-33	175.636	339.979	350.319	−1.2	18,785.6	18,158.6	40.583	.104
7-21-33	161.675	339.958	349.959	−4.0	17,576.5	17,578.2	40.498	.019
Even-temperature interval t_1 to t_2=340 to 350°. $Z]_{340}^{350}$=11,030.7 int. j. Mean value of $\alpha]_{340}^{350}$=40.479 int. j/g.								
7-21-33	161.675	349.959	360.051	−3.0	18,391.9	18,224.0	40.495	.023
7-24-33	154.806	350.031	360.051	−2.7	17,973.4	17,933.6	40.416	−.056
7-25-33	83.182	350.024	360.168	−0.7	15,270.3	15,045.2	40.493	.021
7-26-33	140.531	350.085	360.037	−5.6	17,293.9	17,373.4	40.536	.064
7-27-33	140.044	349.944	360.067	−4.8	17,518.5	17,304.4	40.184	−.288
9-28-33	94.582	350.046	360.034	−0.6	15,471.6	15,487.6	40.290	−.182
10-5-33	81.038	350.032	360.301	−6.9	15,395.1	14,977.7	40.732	.260
10-6-33	81.557	350.023	360.244	−6.5	15,337.7	14,995.2	40.687	.215
10-9-33	139.949	350.038	360.294	−14.2	17,814.8	17,355.5	40.576	.104
Even-temperature interval t_1 to t_2=350 to 360°. $Z]_{350}^{360}$=11,676.9 int. j. Mean value of $\alpha]_{350}^{360}$=40.472 int. j/g.								
7-26-33	140.531	360.037	369.738	−33.6	17,878.3	18,449.2	40.652	.116
7-27-33	140.044	360.067	369.930	−23.7	18,139.9	18,393.3	40.394	−.142
9-28-33	94.582	360.034	369.821	−10.2	16,193.6	16,560.2	40.428	−.108
10-5-33	81.038	360.306	370.164	−39.8	15,814.2	16,011.1	40.409	−.127
10-6-33	81.557	360.244	369.978	−34.2	15,625.2	16,039.7	40.503	−.033
10-9-33	139.949	360.294	369.866	−19.1	17,654.4	18,436.4	40.729	.193
Even-temperature interval t_1 to t_2=360 to 370°. $Z]_{360}^{370}$=12,736.4 int. j. Mean value of $\alpha]_{360}^{370}$=40.536 int. j/g.								
1-17-33	45.854	99.960	150.153	.....	43,129.2	42,960.3	208.466	−.216
1-18-33	45.854	99.966	150.181	.....	43,162.2	42,973.8	208.760	.078
1-19-33	45.854	100.062	149.796	.....	42,724.7	42,956.0	208.372	−.310
1-21-33	218.231	100.196	149.730	.....	78,184.1	78,922.6	208.592	−.090
1-23-33	218.231	99.950	149.363	.....	77,977.9	78,920.0	208.580	−.102
1-24-33	218.231	100.003	149.743	.....	78,557.3	78,972.9	208.823	.141
1-25-33	218.231	99.984	150.168	.....	79,242.6	78,949.2	208.714	.032
1-26-33	61.155	99.978	150.149	.....	46,349.2	46,189.0	209.103	.421
1-27-33	61.155	100.052	150.241	.....	46,340.7	46,189.8	208.626	−.056
Group *I*. $Z]_{100}^{150}$=33,401.3 int. j. $\alpha]_{100}^{150}$=208.682 int. j/g=α_m.								
5-9-33	221.000	99.990	149.766	−5.4	79,123.9	79,484.8	208.542	−.025
5-10-33	125.970	100.070	150.037	−2.9	59,638.5	59,676.3	208.616	.049
5-11-33	59.989	100.105	150.143	−1.6	45,947.2	45,907.0	208.538	−.029
5-12-33	59.989	100.062	150.371	−1.2	46,198.2	45,905.4	208.512	−.055
5-24-33	175.965	100.057	150.128	0.7	70,205.6	70,101.8	208.591	.024
5-25-33	56.864	99.914	150.440	−1.3	45,741.6	45,257.2	208.571	.004
Group *II*. $Z]_{100}^{150}$=33,397.0 int. j. $\alpha]_{100}^{150}$=208.567 int. j/g=α_m. Even-temperature interval t_1 to t_2=100 to 150°. Combined mean value of $\alpha]_{100}^{150}$=208.605 int. j/g.								
1-17-33	45.854	150.153	199.449	.....	44,737.1	45,389.0	207.834	−.276
1-19-33	45.854	149.796	200.029	.....	45,586.3	45,379.9	207.635	−.475
1-23-33	218.231	149.363	200.055	.....	82,390.6	81,279.4	208.130	.020
1-24-33	218.231	149.743	199.488	.....	80,838.3	81,275.6	208.113	.003
1-25-33	218.231	150.168	199.659	.....	80,433.7	81,266.9	208.073	−.037
1-26-33	61.155	150.149	199.820	.....	48,276.4	48,598.0	208.307	.197
1-27-33	61.155	150.241	200.406	.....	48,791.5	48,611.7	208.531	.421
Group *I*. $Z]_{100}^{200}$=35,859.0 int. j. $\alpha]_{100}^{200}$=208.110 int. j/g=α_m.								

TABLE 1.—*Principal data from α experiments*—Continued

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Entire energy added Q	Energy for even temperature interval $Q]_{t_1}^{t_2}$	$\alpha]_{t_1}^{t_2}$	Deviation $\alpha]_{t_1}^{t_2}-\alpha_m$
	g	°C	°C	*Int.* j	*Int.* j	*Int* j	*Int.* j/g	*Int.* j/g
5-9-33	221.000	149.766	199.851	−3.0	81,947.7	81,820.5	208.014	−0.133
5-10-33	125.970	150.037	200.019	−0.7	62,055.7	62,076.6	208.203	.066
5-11-33	59.989	150.143	200.110	−2.9	48,296.4	48,321.0	207.900	−.237
5-12-33	59.989	150.371	200.187	−1.2	48,168.2	48,330.1	208.051	−.086
5-23-33	253.166	150.158	200.341	0.7	88,908.2	88,569.5	208.244	.107
5-24-33	175.965	150.128	200.131	−.2	72,518.4	72,507.3	208.326	.189
5-25-33	56.864	150.440	200.140	−2.4	47,418.2	47,688.0	208.193	.056
Group *II.* $Z]_{150}^{200}=35,849.3$ int. j. $\alpha]_{150}^{200}=208.137$ int. j/g$=\alpha_m$. Even-temperature interval t_1 to t_2=150 to 200°. Combined mean value of $\alpha]_{150}^{200}=208.128$ int. j/g.								
1-17-33	45.854	199.449	249.579	.....	48,874.9	48,786.3	206.545	−.496
1-19-33	45.854	200.029	250.725	.....	49,498.9	48,787.7	206.575	−.466
1-23-33	218.231	200.055	249.858	.....	84,146.3	84,483.8	206.975	−.066
1-24-33	218.231	199.488	249.738	.....	84,894.6	84,501.1	207.054	.013
1-25-33	218.231	199.659	249.850	.....	84,782.3	84,476.9	206.944	−.097
1-26-33	61.155	199.820	250.156	.....	52,342.7	51,993.1	207.304	.263
1-27-33	61.155	200.406	249.960	.....	51,540.9	51,991.8	207.283	.242
2-3-33	158.636	199.951	249.846	.....	72,046.4	72,205.3	207.329	.288
Group *I.* $Z]_{200}^{250}=39,315.4$ int. j. $\alpha]_{200}^{250}=207.041$ int. j/g$=\alpha_m$.								
5-9-33	221.000	199.851	250.158	−.6	85,538.6	85,014.7	206.819	−.182
5-10-33	125.970	200.019	249.921	−1.6	65,279.6	65,410.1	207.210	.209
5-11-33	59.989	200.110	250.109	−0.1	51,719.2	51,711.7	206.770	−.231
5-12-33	59.989	200.187	250.082	.4	51,616.4	51,714.5	206.816	−.185
5-23-33	253.166	200.341	249.825	−3.0	90,864.2	91,806.4	207.368	.367
5-24-33	175.965	200.131	250.011	−2.5	75,600.0	75,776.1	207.247	.246
5-25-33	56.864	200.141	249.918	−5.1	50,838.2	51,074.7	206.931	−.070
Group II. $Z]_{200}^{250}=39,307.8$ int. j. $\alpha]_{200}^{250}=207.001$ int. j/g$=\alpha_m$. Even-temperature interval t_1 to t_2=200 to 250°. Combined mean value of $\alpha]_{200}^{250}=207.014$ int. j/g.								
1-17-33	45.854	249.579	299.461	.....	53,243.7	53,418.9	204.883	−.896
1-19-33	45.854	250.725	299.625	.....	52,268.2	53,426.9	205.057	−.721
1-23-33	218.231	249.858	299.708	.....	88,657.9	88,947.8	205.853	.075
1-24-33	218.231	249.738	300.137	.....	89,632.3	88,927.5	205.760	−.018
1-25-33	218.231	249.850	299.643	.....	88,513.3	88,908.4	205.673	−.105
1-26-33	61.155	250.156	300.022	.....	56,490.3	56,619.4	205.955	.177
1-27-33	61.155	249.960	299.818	.....	56,458.5	56,631.8	206.158	.380
2-6-33	158.636	250.276	300.285	.....	76,695.4	76,650.8	205.670	−.108
2-7-33	158.636	249.990	299.507	.....	75,914.8	76,683.5	205.876	.098
2-8-33	71.459	250.008	299.831	.....	58,545.5	58,763.0	206.255	.477
2-10-33	71.459	249.999	299.955	.....	58,691.6	58,746.1	206.019	.241
2-14-33	223.502	249.932	299.868	.....	89,891.3	90,016.7	205.781	.003
Group II. $Z]_{250}^{300}=44,024.2$ int. j. $\alpha]_{250}^{300}205.778$ int. j/g$=\alpha_m$.								
5-10-33	125.970	249.921	299.914	−0.3	69,915.1	69,933.4	206.159	−.066
5-11-33	59.989	250.109	299.708	−.1	55,875.0	56,337.8	206.276	.051
5-12-33	59.989	249.764	299.848	−2.1	56,428.0	56,354.8	206.560	.335
5-24-33	175.965	250.011	299.623	−0.3	79,612.8	80,256.1	206.249	.024
5-25-33	56.864	249.918	300.076	−11.2	55,859.0	55,671.3	205.891	−.334
Group II. $Z]_{250}^{300}=43,963.5$ int. j. $\alpha]_{250}^{300}=206.225$ int. j/g$=\alpha_m$. Even-temperature interval t_1 to t_2=250 to 300°. Combined mean value of $\alpha]_{250}^{300}=206.076$ int. j/g.								
1-26-33	61.155	300.022	325.087	.....	30,738.8	30,668.6	101.920	−.083
1-27-33	61.155	299.818	324.898	.....	30,744.1	30,656.8	101.727	−.266
2-2-33	61.220	299.965	324.993	.....	30,713.7	30,681.3	102.019	.046
2-6-33	158.636	300.285	325.389	.....	40,805.9	40,611.5	101.968	−.005
2-7-33	158.636	299.507	324.796	.....	41,067.2	40,622.8	102.039	.066
2-8-33	71.459	299.831	325.169	.....	32,159.2	31,728.7	102.059	.086
2-10-33	71.459	299.955	325.345	.....	32,236.0	31,727.5	102.042	.069
2-14-33	164.242	299.894	325.258	.....	41,817.7	41,210.8	102.136	.163
2-15-33	185.040	300.015	324.820	.....	42,947.7	43,291.5	101.901	−.072
2-16-33	176.362	299.880	325.047	.....	42,681.8	42,400.8	101.865	−.108
Group I. $Z]_{300}^{325}=24,435.7$ int. j. $\alpha]_{300}^{325}=101.973$ int. j/g$=\alpha_m$.								

TABLE 1.—*Principal data from α experiments*—Continued

Date	Mass of water, M	Initial temperature	Final temperature	Heat leak	Entire energy added Q	Energy for even temperature interval $Q]_{t_1}^{t_2}$	$\alpha]_{t_1}^{t_2}$	Deviation $\alpha]_{t_1}^{t_2}-\alpha_m$
	g	°C	°C	*Int.* j	*Int.* j	*Int.* j	*Int.* j/g	*Int.* j/g
1-26-33	61.155	325.087	349.478	.....	32,110.1	32,937.1	101.390	−0.040
1-27-33	61.155	324.898	350.036	.....	33,123.2	32,943.6	101.496	.066
2-2-33	61.220	324.991	349.953	.....	32,887.5	32,940.0	101.330	−.100
2-6-33	158.636	325.389	349.758	.....	41,755.8	42,833.8	101.473	.043
2-7-33	158.636	324.796	349.757	.....	42,736.6	42,828.9	101.442	.012
2-8-33	71.459	325.169	350.221	.....	34,109.9	34,016.0	101.868	.438
2-10-33	71.459	325.345	349.811	.....	33,244.1	33,965.4	101.160	−.270
2-14-33	164.242	325.258	350.479	.....	43,765.8	43,338.3	101.081	−.349
2-15-33	185.040	324.820	349.738	.....	45,357.2	45,530.4	101.566	.136
2-16-33	176.362	325.047	349.691	.....	43,986.8	44,640.7	101.519	.089
Group I. $Z]_{325}^{350}=26{,}736.6$ int. j. $\alpha]_{325}^{350}=101.430$ int. j/g$=\alpha_m$.								
5-10-33	125.970	299.914	349.572	−0.7	76,186.6	76,765.7	204.204	.158
5-11-33	59.989	299.706	349.927	−.8	63,536.0	63,290.8	204.182	.136
5-12-33	59.989	299.848	349.973	−1.9	63,437.3	63,294.5	204.244	.198
5-24-33	175.965	299.623	349.756	2.5	87,109.9	86,935.1	203.978	−.068
5-25-33	56.864	300.086	349.933	−11.0	62,424.6	62,617.3	203.559	−.487
Group II. $Z]_{300}^{350}=51{,}042.1$ int. j. $\alpha]_{300}^{350}=204.046$ int. j/g$=\alpha_m$. Even-temperature interval t_1 to t_2=300 to 350°. Combined mean value of $\alpha]_{300}^{350}=203.832$ int. j/g.								

TABLE 2.—*Principal data from β experiments*

Date	Initial temperature	Approximate rate	Mass of liquid removed	Energy corrections	Entire energy added	Corrections to β	β at even temperature	Deviation $\beta-\beta_m$
	°C	g/min	g	*Int.* j/g	*Int.* j/g	*Int.* j/g	*Int.* j/g	*Int* j/g
6-20-33	200.042	4.35	52.031	−48.0	972.8	−0.883	17.814	−0.115
6-20-33	200.063	9.52	171.678	1.1	3,210.6	−.824	17.877	−.052
6-21-33	200.072	9.88	227.568	−18.5	4,285.8	−.910	17.923	−.006
7-7-33	199.983	18.00	89.948	−67.0	1,728.8	−1.107	18.113	.184
7-10-33	200.024	5.13	102.556	−41.5	1,896.9	−0.580	17.916	−.013
Even temperature 200°. Mean value of β_{200}=17.929 int. j/g.								
7-17-33	230.016	9.70	117.472	−36.7	3,810.2	−1.166	31.269	−.025
7-18-33	230.018	9.72	194.442	−40.8	6,253.0	−0.860	31.302	.008
7-20-33	230.032	9.61	96.091	−50.4	3,093.0	−.876	31.312	.018
Even temperature 230°. Mean value of β_{230}=31.294 int. j/g.								
5-23-33	250.006	9.63	192.688	−9.4	8,630.2	−.747	44.041	−.020
6-6-33	249.989	4.83	193.835	−18.6	8,684.0	−.705	44.096	.035
6-19-33	249.978	4.74	94.972	−28.3	4,248.2	−.684	44.047	−.014
6-19-33	249.993	4.83	96.767	−1.2	4,319.4	−.676	44.061	.000
Even temperature 250°. Mean value of β_{250}=44.061 int. j/g.								
7-13-33	269.999	5.00	84.993	−17.2	5,224.4	−.466	61.003	−.039
7-14-33	270.003	4.95	84.370	−27.3	5,193.4	−.520	61.035	−.007
7-14-33	270.014	4.97	109.412	−7.0	6,741.2	−.549	61.064	.022
7-19-33	270.017	5.00	95.047	−47.3	5,852.4	−.508	61.066	.024
Even temperature 270°. Mean value of β_{270}=61.042 int. j/g.								
5-9-33	299.997	4.74	95.031	−10.1	9,281.7	−.329	97.341	−.113
5-26-33	299.990	4.64	148.481	−301.7	14,671.7	−1.283	97.529	.075
5-29-33	299.976	4.64	148.629	−20.3	14,534.1	−0.311	97.477	.023
7-11-33	299.992	4.75	161.357	21.9	15,781.0	−.332	97.470	.016
Even temperature 300°. Mean value of β_{300}=97.454 int. j/g.								

TABLE 2.—*Principal data from β experiments*—Continued

Date	Initial temperature	Approximate rate	Mass of liquid removed	Energy corrections	Entire energy added	Corrections to β	β at even temperature	Deviation $\beta-\beta_m$
	°C	g/min	g	*Int.* j/g	*Int.* j/g	*Int.* j/g	*Int.* j/g	*Int* j/g
6-2-33	329.976	4.93	118.462	4.9	18,509.6	−0.267	155.982	0.061
7-17-33	330.009	5.00	90.059	0.5	14,064.4	−.339	155.830	−.091
7-19-33	330.007	5.02	85.461	−6.7	13,344.4	−.332	155.814	−.107
7-20-33	330.075	5.03	100.821	−4.5	15,765.3	−.515	155.844	−.077
9-26-33	330.038	5.12	107.511	−6.8	16,808.4	−.422	155.919	−.002
9-28-33	330.012	5.16	103.260	−116.9	16,165.0	−.354	156.193	.272
10-5-33	330.034	5.05	116.103	−19.1	18,139.9	−.414	155.826	−.096
10-6-33	330.051	5.02	115.666	−6.7	18,086.7	−.453	155.957	.036
	Even temperature 330°. Mean value of β_{330}=155.921 int. j/g.							
5-10-33	350.010	5.07	65.981	12.1	14,561.5	−.28	220.41	.32
5-24-33	350.017	4.96	119.101	−4.4	26,271.8	−.38	220.20	.11
7-7-33	349.921	5.06	121.702	−3.8	26,787.8	.01	220.12	.03
7-10-33	350.075	5.02	105.292	−13.8	23,242.3	−.61	220.13	.04
7-13-33	350.019	5.10	86.702	−99.1	19,089.7	−.38	219.80	−.29
1-15-35	350.002	3.42	51.353	3.8	11,308.7	−.40	219.81	−.28
1-18-35	349.997	1.03	21.522	−5.0	4,748.4	−.27	220.36	.27
	Even temperature 350°. Mean value of β_{350}=220.09 int. j/g.							
7-21-33	360.048	4.85	92.233	3.2	24,972.9	−.78	269.98	.05
1-10-35	360.017	3.56	46.290	4.7	12,519.4	−.59	269.86	−.07
1-11-35	360.008	3.58	57.216	5.5	15,475.0	−.53	269.94	.01
	Even temperature 360°. Mean value of β_{360}=269.93 int. j/g.							
7-24-33	364.999	4.80	72.100	−9.6	22,017.9	−.55	304.83	−.47
7-28-33	365.038	4.95	84.277	14.5	25,846.7	−.88	305.78	.48
	Even temperature 365°. Mean value of β_{365}=305.30 int. j/g.							
7-26-33	369.970	5.32	63.792	−38.0	22,966.3	−.29	359.73	.38
7-27-33	370.045	5.17	62.042	4.3	22,416.7	−1.57	359.74	.39
1-29-35	370.001	2.00	9.994	1.4	3,599.3	−0.91	359.25	−.10
2-8-35	369.998	4.00	11.989	−14.2	4,319.5	−.87	359.42	.07
2-8-35	370.003	2.02	14.174	−2.0	5,103.3	−.95	359.09	−.26
2-8-35	370.006	0.39	7.834	18.2	2,803.2	−.99	356.83	−2.52
	Even temperature 370°. Mean value of β_{370}=359.35 int. j/g.							
12-20-34	370.973	2.33	46.592	−7.3	17,511.6	−.58	375.27	.....
	Even temperature 371°. Value of β_{371}=374.29 int. j/g.							
2-11-35	372.003	2.13	14.885	−9.2	5,910.6	−1.46	395.63	0.15
2-11-35	372.006	2.10	16.775	125.9	6,656.3	−1.54	395.26	−.22
2-12-35	371.998	2.90	8.926	−18.0	3,544.4	−1.34	395.73	.25
2-12-35	372.005	0.44	8.737	−2.8	3,463.2	−1.50	394.87	−.61
	Even temperature 372°. Mean value of β_{372}=395.48 int. j/g.							
3-26-34	372.964	5.12	30.602	−75.4	13,128.3	−0.84	428.16	.60
3-27-34	372.997	2.02	26.358	−8.7	11,314.3	−2.05	427.20	−.36
2-14-35	372.997	0.19	10.413	−5.1	4,458.6	−2.03	426.13	−1.43
	Even temperature 373°. Mean value of β_{373}=427.56 int. j/g.							
3-28-34	373.468	1.90	19.009	−18.7	8,660.4	−1.47	454.12	1.77
3-1-35	373.482	0.96	7.699	−45.9	3,539.2	−2.27	457.43	5.08
3-1-35	373.501	.96	7.863	−5.9	3,573.7	−3.32	451.16	−1.19
3-1-35	373.503	.96	7.815	−28.6	3,548.0	−3.43	450.59	−1.76
3-1-35	373.498	.99	7.946	−1.0	3,574.0	−3.17	446.62	−5.73
	Even temperature 373.5°. Mean value of $\beta_{373.5}$=452.35 int. j/g.							
3-29-34	373.761	1.91	9.573	−28.6	4,713.3	−8.00	484.35	.....
2-15-35	373.996	0.53	5.302	291.4	2,685.1	−10.33	496.06	−8.24
2-18-35	374.006	.50	4.996	−16.9	2,519.6	−11.71	492.58	−11.72
2-19-35	373.989	.20	3.886	−7.6	1,980.5	−9.24	500.37	−3.93
2-19-35	373.997	.11	1.736	1.5	919.3	−10.45	519.04	14.74
2-21-35	373.984	.09	1.879	−7.0	944.0	−8.64	493.62	−10.68
2-21-35	373.906	.46	3.242	9.8	1,734.5	−10.35	524.69	20.39
	Even temperature 374°. Mean value of β_{374}=504.30 int. j/g.							

TABLE 3.—*Principal data from γ experiments*

Date	Initial temperature	Approximate rate	Mass of vapor removed	Energy corrections	Entire energy added	Correction to γ	γ at even temperature	Deviation $\gamma-\gamma_{\text{m}}$
	°C	g/min	g	*Int.* j	*Int.* j	*Int.* j/g	*Int.* j/g	*Int.* j/g
5-23-34	100.107	0.24	14.138	−15.6	31,912.3	0.28	2,257.49	−0.30
5-18-34	99.992	1.18	48.369	−145.1	109,184.7	−.02	2,257.30	−.49
	100.002	0.73	36.939	−22.3	83,439.9	.01	2,258.87	1.08
	100.023	1.40	41.871	−28.5	94,538.6	.06	2,257.91	0.12
	99.984	1.01	26.222	−65.7	59,212.7	−.04	2,258.09	.30
5-23-34	100.036	1.01	26.246	19.1	59,260.6	.09	2,257.98	.19
	100.003	1.01	26.209	−21.3	59,179.3	.01	2,257.99	.20
	100.046	0.60	14.906	31.6	33,647.0	.12	2,257.40	−.39
	99.997	.59	23.679	−21.8	53,450.8	−.01	2,257.30	−.49
5-28-34	100.005	.59	17.750	−18.6	40,071.0	.01	2,257.53	−.26
	100.022	1.03	30.853	−37.3	69,660.7	.06	2,257.89	.10
5-29-34	100.025	0.73	21.856	−2.8	49,336.6	.06	2,257.41	−.38
	100.032	1.27	25.329	−30.8	57,187.0	.08	2,257.85	.06
	Even temperature 100°. Mean value of γ_{100}=2,257.79 int. j/g							
	150.004	1.19	35.629	−27.1	75,522.1	.01	2,119.69	.19
5-31-34	150.026	1.48	44.475	−5.7	94,256.5	.08	2,119.39	−.11
	150.030	1.48	44.429	−1.4	94,163.4	.09	2,119.50	.00
	150.002	0.98	29.358	−24.7	62,225.7	.01	2,119.56	.06
6-1-34	150.023	.58	17.566	1.8	37,234.2	.07	2,119.74	.24
	150.019	.58	17.551	−9.7	37,200.2	.06	2,119.61	.11
	150.021	1.75	52.456	−5.0	111,168.9	.06	2,119.34	−.16
	Even temperature 150°. Mean value of γ_{150}=2,119.50 int. j/g							
	200.004	1.84	36.849	−16.4	72,115.5	.01	1,957.06	−.05
6-4-34	200.014	1.84	36.793	−2.9	72,008.0	.05	1,957.16	.05
	200.016	0.53	15.819	2.0	30,951.4	.06	1,956.66	−.45
	200.014	0.53	15.812	−8.0	30,941.9	.05	1,956.91	−.20
	199.991	1.43	28.504	−16.7	55,780.2	−.03	1,956.90	−.21
6-5-34	200.002	1.43	28.485	2.4	55,754.7	.01	1,957.35	.24
	199.998	.93	18.676	−8.4	36,552.4	−.01	1,957.18	.07
	200.004	.93	37.345	6.3	73,097.4	.01	1,957.36	.25
	Even temperature 200°. Mean value of γ_{200}=1,957.11 int. j/g							
	249.905	1.05	39.918	−11.2	70,192.9	−.42	1,758.12	−.62
1-31-34	249.905	1.05	22.054	10.0	38,803.5	−.42	1,759.17	.43
	249.931	2.01	64.231	−9.2	112,917.3	−.31	1,757.67	−1.07
2-1-34	249.931	2.01	60.170	17.2	105,838.0	−.31	1,758.73	−0.01
	249.948	0.52	14.581	−3.5	25,652.9	−.24	1,759.36	.62
	249.948	.52	15.622	2.9	27,476.3	−.24	1,758.84	.10
	249.948	.52	15.615	−0.4	27,472.4	−.24	1,759.38	.64
	249.948	.52	15.614	−2.5	27,464.3	−.24	1,758.97	.23
2-2-34	249.948	.52	15.606	−11.7	27,450.2	−.24	1,758.97	.23
	249.948	.52	15.598	−4.2	27,451.0	−.24	1,759.93	1.19
	249.948	.52	15.598	−2.6	27,448.1	−.24	1,759.73	0.99
	249.948	.52	15.599	7.5	27,454.2	−.24	1,760.02	1.28
	249.948	.52	15.602	−0.9	27,443.6	−.24	1,759.00	0.26
	250.002	2.04	40.791	5.8	71,725.7	.01	1,758.45	−.29
2-26-34	250.006	2.04	40.755	−4.4	71,638.8	.03	1,757.89	−.85
	250.005	2.04	40.711	2.3	71,585.0	.02	1,758.46	−.28
	250.007	2.04	30.508	5.2	53,659.0	.03	1,758.95	.21
	250.000	2.05	41.047	−20.6	72,189.6	.00	1,758.70	−.04
6-6-34	250.015	2.05	41.000	14.4	72,124.8	.07	1,759.21	.47
	250.007	0.52	20.778	−3.1	36,539.4	.03	1,758.59	−.15
	250.009	1.57	31.447	−0.8	55,316.4	.04	1,759.08	.34
	249.996	1.44	28.689	−8.4	50,469.9	−.02	1,759.19	.45
6-7-34	250.003	1.44	28.667	23.1	50,424.7	.01	1,758.99	.25
	249.986	.83	25.029	−18.0	44,023.5	−.06	1,758.84	.10
	Even temperature 250°. Mean value of γ_{250}=1,758.74 int. j/g.							
	270.021	1.02	20.376	5.0	33,916.1	.10	1,664.79	.08
	270.016	1.02	20.364	−2.5	33,905.6	.08	1,665.24	.53
3-8-34	270.014	1.02	20.364	−12.4	33,890.4	.07	1,664.48	−.23
	270.015	1.02	20.368	0.2	33,898.8	.07	1,664.57	−.14
	270.017	1.02	20.363	6.9	33,899.1	.09	1,665.01	.30
	270.018	1.02	20.369	6.3	33,892.8	.09	1,664.21	−.50
	270.007	2.03	40.690	−2.3	67,733.2	.04	1,664.75	.04
3-13-34	270.009	2.03	40.659	−2.6	67,680.6	.05	1,664.73	.02
	270.008	2.03	54.856	8.0	91,309.1	.04	1,664.65	−.06
	Even temperature 270°. Mean value of γ_{270}=1,664.71 int. j/g.							

TABLE 3.—*Principal data from γ experiments*—Continued

Date	Initial temperature	Approximate rate	Mass of vapor removed	Energy corrections	Entire energy added	Correction to γ	γ at even temperature	Deviation $\gamma-\gamma_m$
	°C	g/min	g	*Int.* J	*Int.* J	*Int.* J/g	*Int.* J/g	*Int.* J/g
2-14-34	290.021	1.97	39.384	−1.5	61,402.9	0.12	1,559.33	−0.09
	290.020	1.97	31.495	2.5	49,104.5	.11	1,559.36	−.06
	290.022	1.97	39.358	8.0	61,367.0	.12	1,559.45	.03
2-15-34	290.021	1.02	25.500	1.4	39,760.5	.12	1,559.59	.17
	290.021	1.02	25.483	−1.2	39,726.1	.12	1,559.29	−.13
	290.020	1.02	25.459	−1.7	39,693.9	.11	1,559.48	.06
	290.022	1.02	20.357	3.0	31,738.4	.12	1,559.45	.03
	290.025	1.02	21.370	14.5	33,318.4	.14	1,559.50	.08
	Even temperature 290°. Mean value of γ_{290}=1,559.42 int. J/g.							
2-16-34	300.012	2.02	40.403	−1.0	60,665.5	.07	1,501.72	.27
	300.011	2.02	40.510	−0.9	60,809.4	.07	1,501.31	−.14
	300.012	2.02	44.511	6.6	66,822.3	.07	1,501.46	.01
2-19-34	300.013	2.00	40.010	0.2	60,052.7	.08	1,501.16	−.29
	300.016	2.00	40.028	1.7	60,075.4	.10	1,501.07	−.38
	300.017	2.00	43.981	1.0	66,011.1	.10	1,501.14	−.31
6-8-34	300.005	1.05	20.971	−0.6	31,495.8	.03	1,501.90	.45
	300.008	1.05	26.195	2.6	39,329.1	.05	1,501.45	.00
	300.010	0.73	29.403	13.2	44,149.2	.06	1,501.58	.13
6-11-34	300.004	2.30	50.622	7.4	76,012.7	.03	1,501.60	.15
	300.012	1.74	36.592	4.1	54,956.3	.07	1,501.94	.49
	300.015	0.72	34.722	18.5	52,134.9	.09	1,501.58	.13
	Even temperature 300°. Mean value of γ_{300}=1,501.45 int. J/g.							
2-20-34	309.999	1.95	39.010	−0.5	56,117.2	−.01	1,438.68	.00
	310.001	1.95	39.000	−2.5	56,088.7	.01	1,438.34	−.34
	310.003	1.95	44.840	4.5	64,500.5	.02	1,438.64	−.04
2-21-34	310.008	1.99	39.826	5.9	57,297.4	.06	1,438.91	.23
	310.007	1.99	39.805	−3.1	57,264.8	.05	1,438.84	.16
	310.012	1.99	43.785	3.6	62,982.7	.08	1,438.69	.01
	Even temperature 310°. Mean value of γ_{310}=1,438.68 int. J/g.							
2-28-34	320.018	1.82	36.540	5.5	50,070.3	.13	1,370.63	.10
	320.017	1.82	27.374	−2.5	37,508.6	.12	1,370.56	.03
	320.018	1.82	32.815	3.6	44,972.6	.13	1,370.83	.30
3-1-34	320.024	1.98	39.524	−1.1	54,145.7	.17	1,370.35	−.18
	320.024	1.98	39.513	−0.2	54,133.6	.17	1,370.43	−.10
	320.028	1.98	39.519	2.9	54,137.7	.20	1,370.36	−.17
	Even temperature 320°. Mean value of γ_{320}=1,370.53 int. J/g							
3-2-34	330.015	2.01	38.238	1.1	49,517.2	.12	1,295.33	−.02
	330.018	2.01	38.220	−0.8	49,497.9	.14	1,295.46	.11
	330.021	2.01	38.218	1.6	49,485.8	.17	1,295.24	−.11
	Even temperature 330°. Mean value of γ_{330}=1295.35 int. J/g.							
3-5-34	340.017	2.01	36.097	−1.3	43,688.4	.15	1,210.70	−.51
	340.017	2.01	36.077	−0.7	43,663.2	.15	1,210.67	−.54
	340.017	2.01	31.575	−3.6	38,265.1	.15	1,212.27	1.06
	Even temperature 340°. Mean value of γ_{340}=1211.21 int. J/g.							

TABLE 3.—*Principal data from γ experiments*—Continued

Date	Initial temperature	Approximate rate	Mass of vapor removed	Energy corrections	Entire energy added	Correction to γ	γ at even temperature	Deviation γ−γ₃₅₀
	°C	g/min	g	*Int.* j	*Int.* j	*Int.* j/g	*Int.* j/g	*Int.* j/g
3-6-34	350.025	2.03	40.538	−2.1	45,057.8	0.27	1,112.04	−0.34
	350.025	2.03	40.528	−3.3	45,038.7	.27	1,111.84	−.54
6-25-34	350.025	2.96	44.313	−16.4	49,256.3	.27	1,111.82	−.56
	350.032	1.82	36.202	19.6	40,352.4	.35	1,112.23	−.15
10-17-34	349.970	2.02	40.565	−18.7	45,136.6	−.33	1,112.37	−.01
	349.973	0.086	4.312	−22.3	4,797.8	−.29	1,112.37	−.01
1-15-35	349.993	.48	4.768	−11.6	5,308.9	−.08	1,113.27	.89
	349.996	3.21	32.110	−10.2	35,711.1	−.05	1,112.09	−.29
	349.997	0.061	1.820	−10.8	2,024.8	−.03	1,112.31	−.07
	349.996	1.08	10.814	−8.9	12,038.1	−.04	1,113.10	.72
1-16-35	349.999	1.55	3.092	−7.0	3,438.1	−.01	1,112.10	−.28
	350.010	1.06	10.644	−10.1	11,847.3	.11	1,113.19	.81
	350.016	0.50	4.967	−2.0	5,533.6	.17	1,114.20	1.82
1-18-35	350.002	.063	1.893	−12.2	2,106.6	.03	1,112.87	0.49
	350.004	.18	3.589	−10.6	3,991.0	.05	1,112.06	−.32
	349.996	.48	4.766	−6.3	5,304.9	−.05	1,113.02	.64
	349.993	.17	3.512	−9.7	3,904.8	−.08	1,111.73	−.65
	349.997	3.26	32.602	−8.4	36,261.1	−.03	1,112.22	−.16
1-21-35	349.998	0.16	3.203	−6.4	3,565.1	−.02	1,113.06	.68
	349.998	1.01	10.152	0.5	11,301.0	−.02	1,113.10	.72
	349.991	0.17	3.365	−3.6	3,750.5	−.10	1,114.33	1.95
	349.987	.17	3.360	−16.6	3,737.7	−.14	1,112.20	−0.18
	349.990	.17	3.358	−13.7	3,738.4	−.10	1,113.14	.76
	349.991	.17	3.362	−9.7	3,742.2	−.09	1,113.03	.65

Even temperature 350°. Mean value of γ_{350}=1112.38 int. j/g.

3-8-34	360.017	2.05	40.996	−12.0	40,507.6	.25	988.68	−.44
	360.022	2.04	38.939	−5.0	38,473.9	.32	988.72	−.40
3-9-34	360.002	2.96	29.664	−0.1	39,331.7	.03	989.17	.05
3-12-34	360.008	3.69	40.631	−2.0	40,161.0	.12	988.72	−.40
	360.000	3.69	36.902	−1.5	36,474.0	.00	988.57	−.55
10-23-34	359.979	3.51	38.603	−11.6	38,191.4	−.31	989.03	−.09
	359.979	0.038	2.033	−42.5	2,007.0	−.30	986.91	−2 21
	359.983	3.58	35.807	−8.1	35,425.8	−.25	989.10	−0.02
10-24-34	359.982	0.038	1.968	−37.1	1,939.8	−.27	985.40	−3.72
	359.985	3.60	36.043	−13.0	35,653.8	−.22	988.98	−0.14
1-10-35	359.985	0.11	3.400	−14.1	3,375.9	−.22	992.69	3.57
	360.010	.55	10.925	−10.1	10,810.4	.14	989.61	0.49
	360.011	3.66	36.636	−6.8	36,242.3	.16	989.42	.30
1-11-35	360.014	0.074	2.208	−2.8	2,185.6	.21	990.02	.90
	360.017	.18	3.638	0.9	3,597.8	.25	989.17	.05
	360.001	.067	2.008	−11.3	1,995.3	.02	993.50	4.38
1-22-35	360.006	3.66	36.594	−3.2	36,192.4	.08	989.12	0.00
	360.008	0.54	5.430	1.6	5,371.4	.11	989.37	.25
	359.993	.34	6.829	−2.8	6,765.7	−.10	990.63	1.51
	359.995	.34	6.824	−3.4	6,757.6	−.07	990.26	1.14
1-24-35	359.999	.34	6.827	1.8	6,759.2	−.02	990.03	0.91
	359.998	.34	6.825	−0.2	6,750.2	−.04	989.01	−.11
	360.002	1.87	18.730	−11.8	18,533.6	.03	989.55	.43
	360.006	1.87	18.697	−1.9	18,494.9	.10	989.31	.19
	360.007	1.87	18.710	−0.5	18,502.0	.10	989.00	−.12
	360.010	1.87	18.704	3.7	18,511.1	.15	989.82	.70

Even temperature 360°. Mean value of γ_{360}=989.12 int. j/g.

3-18-34	365.003	3.95	39.522	6.5	35,925.6	.06	909.26	−.25
	365.002	3.95	27.646	−10.2	25,116.2	.03	908.72	−.79
3-19-34	365.001	0.98	19.601	−10.1	17,815.5	.02	909.63	.12
	365.002	.98	19.526	−14.4	17,745.7	.04	909.56	.05
3-21-34	365.009	.49	9.839	−4.4	8,932.2	.16	909.37	−.14
	365.010	.97	14.570	−9.3	13,232.4	.18	909.08	−.43
1-2-35	365.014	.97	14.558	−7.0	13,226.5	.25	909.50	−.01
	365.016	.39	39.351	1.7	35,783.2	.30	909.63	.12
1-3-35	365.014	.07	1.402	−10.8	1,281.5	.26	914.31	4.80
	365.021	.58	5.841	−12.9	5,314.8	.38	910.29	0.78
	365.007	.58	5.809	−28.3	5,287.5	.13	910.36	.85
1-8-35	365.021	.17	1.733	−26.6	1,582.0	.38	913.25	3.74
	365.001	.57	5.752	−7.0	5,241.4	.02	911.25	1.74
	365.007	3.87	30.970	−3.3	28,160.6	.12	909.41	−0.10
	365.013	0.078	2.332	−4.2	2,125.4	.23	911.64	2.13

Even temperature 365°. Mean value of γ_{365}=909.51 int. j/g

TABLE 3.—*Principal data from γ experiments*—Continued

Date	Initial temperature	Approximate rate	Mass of vapor removed	Energy corrections	Entire energy added	Correction to γ	γ at even temperature	Deviation $\gamma-\gamma_a$
	°C	g/min	g	*Int.* j	*Int.* j	*Int.* j/g	*Int.* j/g	*Int.* j/g
	369.978	0.56	11.268	−11.8	9,020.2	−0.62	801.16	0.72
3-16-34	369.986	.56	9.938	−13.0	7,934.4	−.39	799.27	−1.17
	369.993	.56	6.962	−2.1	5,569.7	−.20	801.06	0.62
	369.959	4.60	36.746	27.5	29,507.5	−1.14	801.87	1.43
10-26-34	369.947	0.14	4.108	−31.9	3,298.3	−1.50	801.40	0.96
	370.020	.088	1.756	5.8	1,410.6	0.56	803.86	3.42
12-17-34	370.017	.56	11.249	2.8	9,007.3	.48	801.20	0.76
	370.004	.20	4.097	−1.5	3,283.7	.11	801.63	1.19
	370.006	.20	4.109	6.8	3,293.6	.16	801.20	0.76
1-28-35	370.006	.20	4.108	−0.2	3,291.8	.16	801.96	1.52
	370.006	.20	4.113	−.4	3,298.2	.18	801.94	1.50
	370.003	1.87	9.383	−6.6	7,510.9	.09	800.49	0.05
	370.007	1.87	9.387	−3.3	7,510.1	.20	800.16	−.28
1-29-35	370.008	1.87	9.390	3.2	7,501.8	.24	799.78	−.66
	370.007	1.87	18.724	2.2	14,977.1	.19	799.98	−.46
	370.003	3.26	12.777	−6.7	10,218.4	.10	799.85	−.59
2-6-35	370.006	3.26	12.788	−0.1	10,225.9	.18	799.82	−.62
	370.005	3.26	12.787	4.6	10,233.2	.15	800.46	.02
	Even temperature 370°. Mean value of γ_{370}=800.44 int. j/g.							
	372.002	0.45	9.027	−8.8	6,593.2	.08	732.07	−1.88
	372.007	.45	9.014	−9.2	6,582.8	.28	734.19	0.24
3-20-34	372.005	.93	9.267	−7.3	6,766.6	.20	731.18	−2.77
	372.006	.93	9.267	−4.0	6,770.8	.24	731.66	−1.99
	371.990	4.85	24.230	35.4	17,849.6	−.40	736.27	2.62
12-18-34	371.970	0.09	1.804	−55.6	1,340.7	−1.22	741.96	8.31
	372.000	.72	10.143	2.5	7,446.2	0.00	734.12	0.47
	372.006	.20	4.050	−5.9	2,978.4	.24	735.63	1.98
2-11-35	372.007	.20	4.057	−1.1	2,982.2	.29	735.35	1.70
	372.007	2.90	14.520	−1.6	10,634.8	.27	732.67	−0.98
2-12-35	372.008	2.90	14.519	13.4	10,618.2	.34	733.02	−.63
	371.998	1.96	9.816	1.1	7,204.5	−.09	733.83	.18
	372.002	1.06	7.408	10.4	5,437.4	.08	734.02	.37
2-13-35	372.002	1.06	7.395	6.2	5,428.7	.06	734.15	.50
	372.002	1.95	9.727	4.6	7,131.1	.07	733.16	−.49
	Even temperature 372°. Mean value of γ_{372}=733.65 int. j/g.							
	373.002	0.60	9.029	2.3	6,154.6	.13	683.00	−.05
	373.002	.60	9.025	3.7	6,152.4	.12	683.05	0.00
3-22-34	373.002	.60	7.986	−37.1	5,289.6	.10	683.68	.63
	373.001	.19	3.892	−2.2	2,666.7	.08	685.20	2.15
2-14-35	373.004	.99	14.839	3.0	10,119.9	.23	682.21	−0.84
	Even temperature 373°. Mean value of γ_{373}=683.05 int. j/g.							
	373.487	.41	8.189	−32.9	5,330.5	−.98	649.97	6.99
	373.504	1.00	8.027	−1.5	5,145.4	.28	641.27	−1.71
2-26-35	373.504	0.39	7.780	1.5	4,993.8	.33	642.19	−0.79
	373.505	.39	7.788	−1.6	4,992.7	.36	641.41	−1.57
	Even temperature 373.5°. Mean value of $\gamma_{373.5}$=642.98 int. j/g.							
	374.015	.19	2.899	3.9	1,728.5	2.44	598.70	12.06
2-18-35	374.016	.52	4.229	3.0	2,420.7	2.56	574.80	−11.82
	373.991	.97	4.728	−3.6	2,828.0	−1.50	596.65	10.03
2-21-35	373.993	.046	0.914	−7.1	540.4	−1.14	590.11	3.49
	373.993	.19	2.870	−12.3	1,747.4	−1.19	607.66	21.04
	374.000	.20	2.981	−15.7	1,742.1	−0.02	584.42	−2.20
2-25-35	374.005	.21	3.094	−0.9	1,756.3	.81	568.40	−18.22
	374.005	.21	3.140	−6.5	1,750.4	.89	558.27	−28.35
	Even temperature 374°. Mean value of γ_{374}=586.62 int. j/g.							

TABLE 5.—*Formulated Data—Saturated Steam—International joules per gram*

Temperature	Latent heat $\gamma-\beta$	$\frac{1}{2}(\gamma+\beta)$	β	γ	$a]_o^t$	Enthalpy liquid H_t-H_o	Enthalpy vapor H'_t-H_o	$T dp/dT$ Int J/cm³
°C								
100	2256. 77		1. 41	2258. 17	417. 36	418. 76	2675. 52	1. 349 38
105	2243. 41		1. 66	2245. 06	438. 21	439. 85	2683. 26	1. 581 33
110	2229. 87		1. 94	2231. 81	459. 06	460. 99	2690. 85	1. 843 94
115	2216. 13		2. 26	2218. 39	479. 91	482. 16	2698. 29	2. 139 95
120	2202. 20	From 330 to 374.15° C values from equation $\frac{1}{2}(\gamma+\beta)=535.08+18.413\ (374.15-t)^{.617}$ From 100 to 330° C values of β are from Smith and Keyes liquid specific-volume data.	2. 62	2204. 82	500. 76	503. 37	2705. 56	2. 472 21
125	2188. 04		3. 03	2191. 07	521. 62	524. 63	2712. 68	2. 843 70
130	2173. 67		3. 48	2177. 16	542. 47	545. 94	2719. 62	3. 257 45
135	2159. 07		3. 99	2163. 06	563. 32	567. 30	2726. 37	3. 716 59
140	2144. 22		4. 56	2148. 78	584. 18	588. 73	2732. 95	4. 224 40
145	2129. 12		5. 19	2134. 31	605. 03	610. 21	2739. 32	4. 784 20
150	2113. 74		5. 89	2119. 63	625. 88	631. 76	2745. 49	5. 399 36
155	2098. 08		6. 66	2104. 74	646. 73	653. 37	2751. 45	6. 073 38
160	2082. 12		7. 50	2089. 62	667. 57	675. 07	2757. 18	6. 809 75
165	2065. 83		8. 44	2074. 27	688. 41	696. 84	2762. 67	7. 612. 11
170	2049. 17		9. 45	2058. 63	709. 25	718. 69	2767. 87	8. 484 10
175	2032. 10		10. 57	2042. 67	730. 08	740. 64	2772. 74	9. 429 51
180	2014. 61		11. 78	2026. 39	750. 91	762. 68	2777. 29	10. 452 1
185	1996. 67		13. 11	2009. 78	771. 72	784. 82	2781. 49	11. 555 6
190	1978. 28		14. 55	1992. 83	792. 53	807. 07	2785. 35	12. 744 1
195	1959. 42		16. 11	1975. 53	813. 33	829. 43	2788. 86	14. 021 3
200	1940. 07		17. 80	1957. 88	834. 13	851. 91	2791. 99	15. 391 3
205	1920. 22		19. 63	1939. 85	854. 91	874. 53	2794. 75	16. 858 5
210	1899. 84		21. 61	1921. 45	875. 68	897. 27	2797. 11	18. 426 5
215	1878. 91		23. 74	1902. 65	896. 43	920. 16	2799. 07	20. 099 8
220	1857. 41		26. 04	1883. 45	917. 18	943. 21	2800. 62	21. 882 6
225	1835. 31		28. 52	1863. 82	937. 91	966. 41	2801. 72	23. 779
230	1812. 58		31. 18	1843. 76	958. 63	989. 80	2802. 38	25. 794
235	1789. 20		34. 04	1823. 24	979. 33	1013. 36	2802. 56	27. 932
240	1765. 13		37. 12	1802. 24	1000. 02	1037. 13	2802. 25	30. 198
245	1740. 33		40. 42	1780. 75	1020. 69	1061. 10	2801. 43	32. 596
250	1714. 77		43. 96	1758. 73	1041. 35	1085. 30	2800. 07	35. 132
255	1688. 40		47. 76	1736. 16	1061. 99	1109. 74	2798. 14	37. 811

250	1714.77		43.96	1758.73	1041.35	1085.30	2800.07	35.132
255	1688.40		47.76	1736.16	1061.99	1109.74	2798.14	37.811
260	1661.17		51.83	1713.01	1082.61	1134.44	2795.61	40.638
265	1633.03		56.21	1689.24	1103.22	1159.41	2792.44	43.619
270	1603.92		60.90	1664.81	1123.81	1184.69	2788.61	46.760
275	1573.75		65.93	1639.68	1144.38	1210.29	2784.05	50.069
280	1542.47		71.33	1613.81	1164.93	1236.25	2778.72	53.550
285	1509.98		77.14	1587.12	1185.46	1262.59	2772.57	57.213
290	1476.17		83.38	1559.55	1205.97	1289.35	2765.52	61.064
295	1440.92		90.11	1531.03	1226.47	1316.57	2757.49	65.113
300	1404.09		97.36	1501.45	1246.94	1344.29	2748.38	69.397
305	1365.50		105.20	1470.70	1267.40	1372.58	2738.08	73.838
310	1324.92		113.68	1438.60	1287.83	1401.50	2726.42	78.537
315	1282.19		122.89	1405.08	1308.25	1431.13	2713.32	83.475
320	1237.24		132.93	1370.18	1328.64	1461.56	2698.81	88.667
325	1189.75		143.92	1333.67	1349.02	1492.93	2682.68	94.130
330	1139.29	725.65	156.00	1295.29	1369.37	1525.36	2664.65	99.882
335	1085.29	712.03	169.39	1254.67	1389.71	1559.08	2644.36	105.946
340	1027.00	697.72	184.22	1211.22	1410.02	1594.23	2621.23	112.355
345	963.38	682.58	200.89	1164.27	1430.31	1631.19	2594.57	119.145
350	892.85	666.42	219.99	1112.84	1450.58	1670.56	2563.42	126.37
355	812.98	648.90	242.41	1055.39	1470.83	1713.23	2526.21	134.10
360	719.43	629.52	269.81	989.23	1491.06	1760.86	2480.28	142.46
365	603.25	607.24	305.62	908.87	1511.27	1816.88	2420.12	151.60
366	575.69	602.27	314.42	890.12	1515.31	1829.72	2405.42	153.55
367	546.04	597.06	324.04	870.08	1519.35	1843.38	2389.42	155.55
368	513.79	591.56	334.66	848.46	1523.39	1858.04	2371.84	157.6
369	478.24	585.70	346.58	824.82	1527.42	1873.99	2352.23	159.7
370	438.30	579.39	360.24	798.54	1531.46	1891.69	2329.99	161.9
371	392.10	572.45	376.40	768.50	1535.49	1911.88	2303.98	164.2
372	336.04	564.61	396.59	732.63	1539.53	1936.11	2272.15	166.6
373	260.98	555.15	424.66	685.64	1543.56	1968.21	2229.19	169.1
374	114.61	540.79	483.49	598.10	1547.59	2031.07	2145.67	172.4
374.15	0.00	535.08	535.08	535.08	1548.20	2083.27	2083.27	173

TABLE 6.—*Properties of saturated steam*

Temperature	Vapor pressure	Enthalpy (International Steam Table cal/g)			Specific Volume (cm³/g)		Entropy (IT cal/g°C)	
		Liquid	Latent heat	Vapor	Liquid	Vapor	Liquid	Vapor
°C	kg/cm²							
100	1. 03323	100. 04	539. 12	639. 2	Below 330° C Smith and Keyes liquid specific volumes used in preference to calorimetric values. Above 330° C values of liquid specific volumes from calorimetric data for β are preferred.	1673. 5	0. 3120	1. 7567
105	1. 2318	105. 08	535. 93	641. 0		1419. 7	. 3254	1. 7426
110	1. 4609	110. 12	532. 69	642. 8		1210. 4	. 3386	1. 7289
115	1. 7239	115. 18	529. 41	644. 6		1036. 7	. 3517	1. 7156
120	2. 0425	120. 25	526. 08	646. 3		891. 8	. 3647	1. 7028
125	2. 3666	125. 33	522. 70	648. 0		770. 5	. 3775	1. 6903
130	2. 7544	130. 42	519. 27	649. 7		668. 36	. 3902	1. 6782
135	3. 1923	135. 52	515. 78	651. 3		582. 00	. 4027	1. 6664
140	3. 6848	140. 64	512. 23	652. 9		508. 66	. 4151	1. 6549
145	4. 2369	145. 77	508. 62	654. 4		446. 12	. 4275	1. 6438
150	4. 8535	150. 92	504. 95	655. 9		392. 57	. 4397	1. 6329
155	5. 5402	156. 08	501. 21	657. 3		346. 55	. 4518	1. 6224
160	6. 3023	161. 27	497. 40	658. 7		306. 86	. 4637	1. 6120
165	7. 1457	166. 47	493. 50	660. 0		272. 50	. 4756	1. 6019
170	8. 0764	171. 69	489. 52	661. 2		242. 65	. 4874	1. 5920
175	9. 1006	176. 93	485. 45	662. 4		216. 63	. 4991	1. 5823
180	10. 2225	182. 20	481. 27	663. 5		193. 87	. 5107	1. 5728
185	11. 456	187. 49	476. 98	664. 5		173. 92	. 5223	1. 5634
190	12. 800	192. 80	472. 59	665. 4		156. 37	. 5337	1. 5541
195	14. 265	198. 14	468. 08	666. 2		140. 90	. 5451	1. 5450
200	15. 857	203. 51	463. 46	667. 0		127. 21	. 5564	1. 5360
205	17. 585	208. 92	458. 72	667. 6		115. 07	. 5677	1. 5270
210	19. 456	214. 35	453. 85	668. 2		104. 28	. 5789	1. 5182
215	21. 477	219. 82	448. 85	668. 7		94. 66	. 5900	1. 5095
220	23. 659	225. 32	443. 71	669. 0		86. 07	. 6011	1. 5009
225	26. 007	230. 87	438. 43	669. 3		78. 380	. 6122	1. 4923
230	28. 531	236. 45	433. 01	669. 5		71. 479	. 6232	1. 4838
235	31. 239	242. 08	427. 42	669. 5		65. 274	. 6342	1. 4753
240	34. 140	247. 76	421. 67	669. 4		59. 681	. 6451	1. 4669
245	37. 244	253. 49	415. 75	669. 2		54. 631	. 6561	1. 4584

240	34.140	247.76	421.67	669.4		39.831	.6451	1.4589
245	37.244	253.49	415.75	669.2		54.631	.6561	1.4584
250	40.560	259.27	409.64	668.9		50.061	.6670	1.4500
255	44.097	265.10	403.34	668.4		45.917	.6779	1.4416
260	47.866	271.00	396.84	667.8		42.153	.6888	1.4331
265	51.875	276.97	390.11	667.1		38.727	.6997	1.4246
270	56.137	283.01	383.16	666.2		35.603	.7106	1.4161
275	60.660	289.13	375.95	665.1		32.749	.7216	1.4074
280	65.457	295.33	368.48	663.8		30.136	.7326	1.3987
285	70.539	301.62	360.72	662.3		27.741	.7436	1.3899
290	75.917	308.01	352.64	660.7		25.540	.7547	1.3809
295	81.603	314.52	344.22	658.7		23.513	.7659	1.3718
300	87.611	321.14	335.42	656.6		21.645	.7772	1.3624
305	93.952	327.90	326.20	654.1		19.918	.7885	1.3528
310	100.64	334.80	316.51	651.3		18.317	.8000	1.3428
315	107.69	341.88	306.30	648.2		16.832	.8117	1.3325
320	115.12	349.15	295.56	644.7		15.453	.8236	1.3219
325	122.95	356.64	284.22	640.9		14.168	.8357	1.3109
330	131.18	364.39	272.16	636.6	1.562	12.968	.8481	1.2993
335	139.85	372.45	259.26	631.7	1.599	11.842	.8609	1.2872
340	148.96	380.85	245.34	626.2	1.640	10.780	.8741	1.2742
345	158.54	389.68	230.14	619.8	1.686	9.77	.8878	1.2601
350	168.63	399.08	213.29	612.4	1.741	8.81	.9023	1.2446
355	179.24	409.27	194.21	603.5	1.808	7.87	.9179	1.2271
360	190.42	420.65	171.86	592.5	1.894	6.94	.9352	1.2066
365	202.21	434.03	144.11	578.1	2.016	6.00	.9554	1.1812
366	204.64	437.10	137.53	574.6	2.048	5.80	.9600	1.1752
367	207.11	440.36	130.44	570.8	2.083	5.59	.9649	1.1687
368	209.60	443.87	122.74	566.6	2.124	5.38	.9702	1.1616
369	212.12	447.68	114.25	561.9	2.170	5.16	.9759	1.1538
370	214.68	451.9	104.71	556.6	2.225	4.93	.9823	1.1451
371	217.26	456.7	93.7	550	2.293	4.68	.9896	1.1350
372	219.88	462.5	80.3	542	2.38	4.40	.9983	1.1228
373	222.53	470.2	62.3	533	2.51	4.05	1.0100	1.1065
374	225.22	485.2	27.4	513	2.80	3.47	1.0329	1.0752
374.15	225.65	498	0	498	3.1	3.1	1.0521	1.0521

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PRECISION CAMERA FOR TESTING LENSES

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ABSTRACT

Apparatus particularly adapted to the testing of airplane camera lenses and complete airplane cameras is described. Seven collimators provide optically distant targets spaced five degrees. These targets are photographed by means of the lens or camera to be tested. An examination and measurement of the resulting negative gives the back focal length, equivalent focal length, and both distortion and quality of definition over the entire field of the lens. This instrument was designed and built for making the tests that are required by all contracts for Government mapping projects.

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I. INTRODUCTION

Shortly after the close of the World War the National Bureau of Standards began testing camera objectives for the U. S. Army Air Corps in order to determine their suitability for use in airplane cameras for mapping projects. The measurements made included determinations of spherical aberration, chromatic aberration, curvature of field, astigmatic difference, and distortion. With the advent of the multiple-lens camera and the increasing utilization of airplane photographs for the construction of topographic maps, the importance of good definition and relative freedom from distortion has become so generally recognized that lenses are seldom installed in airplane cameras without prior measurements of the distortion. The first large lot of airplane lenses received by this Bureau was tested on a bench improvised from parts that were immediately available. A report of these measurements and a description of the apparatus employed have been given by Bennett.[1] When it became evident that airplane camera lenses were to be regularly forwarded to the Bureau for test, a special optical bench adapted to this work was constructed, and this apparatus has also been described.[2] For the measurement of

[1] BS Sci. Pap. 19, 587 (1924) S494.
[2] J. Opt. Soc. Am. & Rev. Sci. Instr. 14, 235 (1927).

the focal length and distortion this bench has proved entirely satisfactory. It is, however, difficult to formulate precise statements regarding the quality of definition of a lens after a bench test has been made, and it is also difficult to determine the value of the back focal length which gives the best average definition over all parts of the field as distinguished from that which gives the best definition on the axis. The precision camera for testing lenses, to be described, was designed and constructed to meet these difficulties and also to expedite the testing of the increasingly large number of airplane camera lenses which is regularly received each year. Not only does this camera

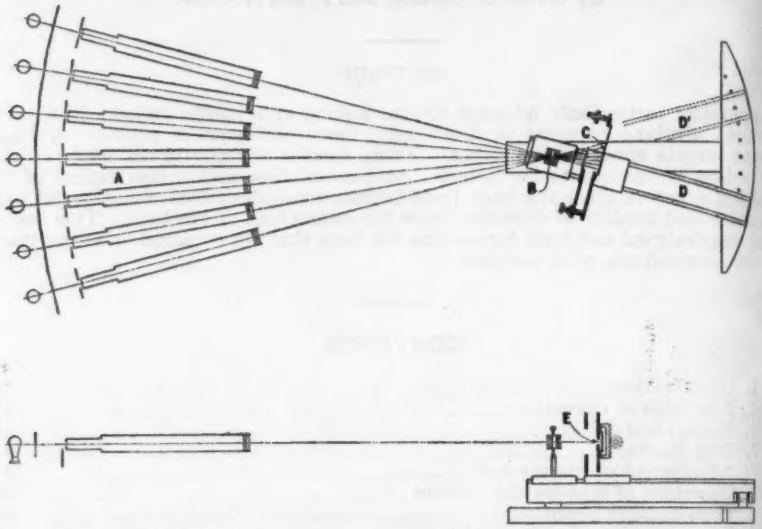

FIGURE 1.—*Schematic representation of the precision camera.*

The seven collimators are at the left, the lens to be tested at *B*, and the photographic plate at *C*.

permit the tests to be made with less expenditure of time and effort, but its use has the further advantage that the negative, made with each lens, constitutes a precise record of the performance of the lens and one which may be preserved for future reference. This apparatus also permits tests to be made on a complete single lens camera with the lens assembled in the camera as it will be when used.

II. PRINCIPLES OF OPERATION

The fundamental elements of the precision camera are shown schematically in plan and in elevation in figure 1. At *A* is a battery of seven collimators, each of which carries a test chart located in the focal plane of its objective and illuminated by transmitted light. The axes of the collimators intersect at *B*, and the angle between any two successive collimators is nominally 5°. The lens to be tested is located at *B*, where it receives light from the seven infinitely distant images as optically presented by the battery of collimators. The images produced by the objective under test are received on the photographic plate at *C*. The lens at *B* and the plate at *C* are carried by a common structure which forms the camera proper. This camera

is rotatable about a point beneath the lens and may be brought into any one of several positions including those indicated as D and D'. When in the position D images are recorded on the photographic plate at 0, 5, 10, 15, 20, 25, and 30° from the axis and for position D' the same is true, except that the images lie on the other side of the axis. Provision is also made for rotating the camera 5° beyond each of the extreme positions shown. This permits the performance of a lens to be tested for a point 35° from the axis. The light reaches the photographic plate through the slot at E, and a mechanism is provided for lowering or raising the plate to permit a series of exposures to be made on a single plate. There is also a slow motion by which the photographic plate may be moved toward or away from the lens through precisely measured distances.

In practice, 19 exposures may be made on a single plate (4 by 10 inches), each one being made with the plate at a different distance from the rear vertex of the lens. The arrangement of the images on the resulting negative is shown in figure 2. All the images in a given vertical column are at a given angular distance from the center

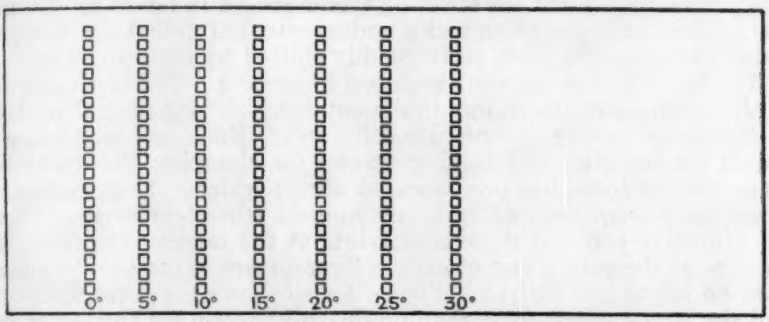

FIGURE 2.—*Schematic drawing of the negative obtained with the precision camera.*

of the field as indicated by the values given on the figure. All of the images in any horizontal row are made by a single exposure and between any two such rows the plate has been withdrawn a definite distance from the lens. The general principle of operation and the arrangement of the images upon the negative is the same as described by Goldberg,[3] although the mechanical construction is entirely different and the addition of the collimators permits lenses of longer focal length to be satisfactorily tested.

Each square represents the image from a collimator as recorded on the negative. The images in a given row are exposed simultaneously and show in the several columns the performance of the lens for each of the indicated angular distances from the center of the field. From exposure to exposure, the distance from the lens to the plate is altered by known amounts. Consequently, each row represents a different focal adjustment, and the one giving the best average definition may be selected as typical of the best performance of the lens.

[3] Sixième Congres International de Photographie, p. 186–193 Paris (1925).

III. MECHANICAL DESIGN

The details of design and construction are well shown in the photographic reproductions of figures 3, 4, and 5. Figure 3 gives a general view of the entire apparatus. The seven collimators are clearly visible at *A*. The camera back at *C* partially hides the chuck at *B* which holds the lens to be tested. The photographic plate rests on two ledges of the aluminum casting carried by the camera back *C*. The ledges extend across the entire back and permit the placing of a plate 4 inches wide, for photographing any portion of the field of the lens, on either side of the axis, without adjustment other than the placing of the plate in the proper position on the two supporting ledges. With this arrangement for holding the plate the room must be darkened during the loading of the camera and it is preferable to keep it dark while the exposures are being made. A loosely fitting cover is provided in order to lessen the danger of stray light reaching the plate during the exposure.

The casting carrying the photographic plate is lowered to present fresh portions of the emulsion for successive exposures. The rack and pinion movement for effecting this is shown in figure 3. On this mechanism an index plate and a spring-actuated detent are also provided to permit the plate to be readily shifted by uniform steps.

The battery of collimators is shown in figure 4. The free apertures of the collimators are 75 mm in diameter, which is greater than those of the lenses commonly submitted for test. Rack and pinion movements for focusing and locking screws for clamping the drawtubes when correct focus has been secured are provided. Each collimator is geometrically mounted with one support (three constraints) under the objective end and three constraints at the target end. The constraints at the target end of each collimator are adjustable to permit it to be aligned as desired. Figure 4 also shows the rotating sectors and the lamps which form the illuminating system for the test charts or targets in each collimator. This portion of the apparatus will be more fully described in section IV.

The camera proper, shown in figure 5, consists of a bed provided with ways, three carriages, and a lead screw. Each carriage is provided with a half-nut, which is normally disengaged from the lead screw but which can be engaged when a slow motion is required for adjustment. Clamps are also provided by which any carriage can be locked in position. The first carriage, nearest the collimator, carries the chuck which receives the lens to be tested; the second carries the camera back; and the third carries a microscope for observing the image. This last carriage also has a vernier applied to the scale carried by the bed. The ways are 121 cm long and lenses with focal lengths lying between 15 and 95 cm can be accommodated.

The bed of the camera is mounted on a vertical spindle at the end nearer the collimators. This spindle is provided with annular and thrust ball bearings. The outer end of the camera bed is carried by two rollers which rotate on ball bearings. These rollers roll on the circular arc clearly visible in figure 3. This circular arc has index holes spaced nominally 5 degrees, and the camera bed carries a corresponding index pin. It is, therefore, possible to lock the camera, by means of this pin, not only in the extreme positions that have been particularly mentioned in section III but also in a series of intermediate positions

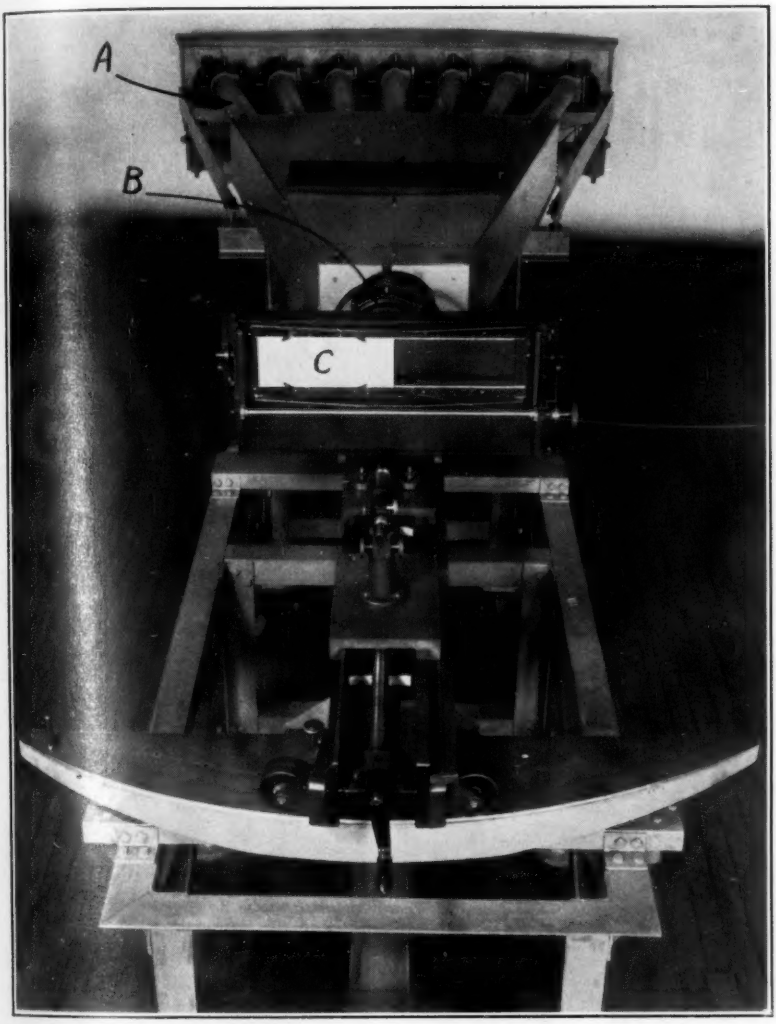

FIGURE 3.—*Complete precision camera.*

The collimators are at *A*, the lens to be tested at *B*, and the photographic plate at *C*.

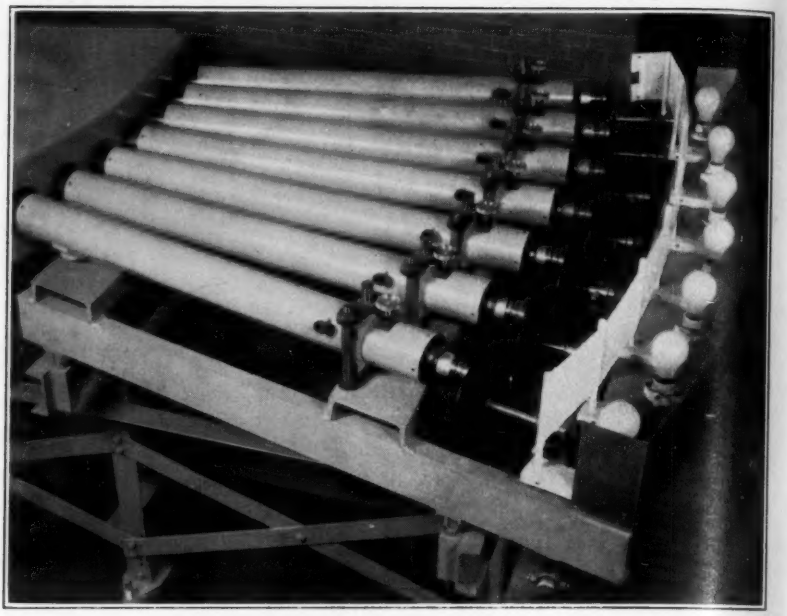

FIGURE 4.—*Collimators, sources of light for illuminating the test charts, and sectored disks for balancing the vignetting of the lens at different angular distances from the center of the field.*

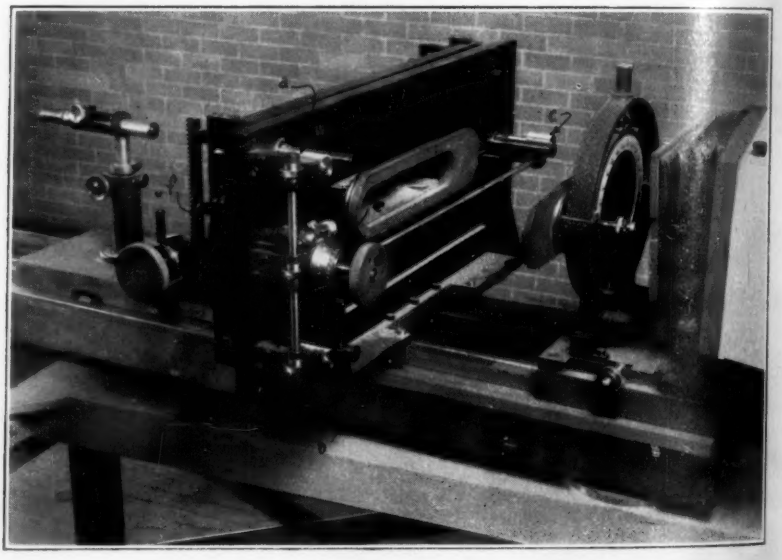

FIGURE 5.—*Lens mount and camera back.*

The carriage at the right carries the chuck that holds the lens to be tested. The central carriage carries the camera back. The spiral gears that actuate the three micrometer screws for obtaining a fine focusing movement and one of the racks that lowers the plate between successive exposures are clearly shown. The third carriage carries a microscope for preliminary focusing.

so that the axis of the camera can be brought into coincidence with the axis of any one of the seven collimators. These intermediate positions are used in adjusting and calibrating the instrument.

The chuck that receives the lens to be tested, shown at the right of figure 5, is mounted to permit translation along or rotation about each of three mutually perpendicular axes, thereby permitting the lens to be centered and adjusted with its axis normal to the photographic plate. The camera back mounted on the center carriage shown in figure 5 consists of two parts. The main part or supporting member is mounted rigidly upon its carriage and carries three micrometer screws at *a*, *b*, and *c*, respectively, which serve to advance the photographic plate. Each micrometer screw carries a long spiral gear and, by a system of smaller gears and shafts, all three micrometer screws are geared together to move equally and simultaneously when the large knurled head at *D* is turned. The shaft upon which *d* is mounted carries a graduated circle for reading fractional turns of the micrometer screws. An index ring also is carried on the same spindle and a spring-actuated detent engaging in the equi-spaced indentations enables one to obtain readily the fractional turns required when advancing the photographic plate between exposures. A Veeder counter at *e* indicates the complete turns of the micrometer screws. The member that carries the plate is held tightly against the three micrometer screws by means of three spiral springs in the three cylindrical spring boxes that can be seen near the three micrometer screws and this member is supported by the crossed rods at *f* and a similar pair of rods on the other side.

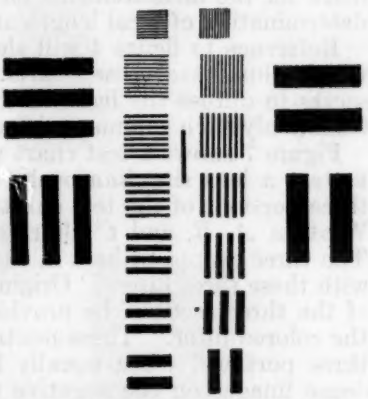

FIGURE 6.—*Test chart for use with monochromatic light.*

For lenses of a given focal length, a series of test charts similar to this, one for each collimator, is provided. These charts are of such size that the number of lines to the millimeter, as recorded on the test plate, form the approximately geometric series 3.5, 5, 7, 10, 14, 20, 28, 40, and 56. The central vertical line is the fiducial mark to which measurements are made for the determination of focal length and distortion.

IV. TEST CHARTS

The test charts for use in the collimators are drawn to a large scale and then photographed to the desired size upon backed process plates. Most of the lenses tested range in focal length from 125 to 250 mm. The focal lengths of the collimator objectives are 1,000 mm and the chart, in most cases, is from 8 to 4 times as large in linear dimensions as the image finally recorded on the photographic plate in the course of a test. As a consequence of this reduction, the test charts produced on photographic plates have been found sufficiently sharp and free from grain to give satisfactory performance.

For testing a lens with monochromatic light the test chart shown in figure 6 has been found satisfactory. The production of a set of these charts is more complicated than might at first appear. If the test charts in all the collimators are identical in size it will be found that the images recorded on the negative at different distances from the axis will not be of the same size. If θ represents the angular

distance of the image from the center of the field, the vertical dimensions of the images at different distances from the axis will vary inversely as cos θ and the horizontal dimensions inversely as $\cos^2\theta$. Furthermore, when lenses of different focal lengths are to be tested, it is desirable to have sets for each focal length to such scale that the patterns on the negatives will be of the same size for all focal lengths. This greatly facilitates a comparison of the definition of image yielded by the different lenses. Consequently, it has been found desirable to make the test charts in focal-length sets of seven, one for each collimator, with the vertical and horizontal dimensions varying according to the ratios cos θ and $\cos^2\theta$ in order that the seven images on a negative may be of the same size. The set of charts for lenses of a given focal length is so made that the lines will be spaced 3.5, 5, 7, 10, 14, 20, 28, 40, and 56 to the millimeter on the test negative.

The vertical bar in the center of the pattern serves as a fiducial mark for the measurements on the negative that are required for the determination of focal length and distortion.

Reference to figure 4 will show the incandescent lamps (60 watts) which illuminate these charts. A single thickness of tracing cloth serves to diffuse the light so that the chart is uniformly illuminated. Commonly each collimator is provided with a K3 gelatine filter.

Figure 7 shows a test chart which has been used when it is desired to test a lens simultaneously for light of three wave lengths. The three portions of the test chart lettered *A*, *B*, and *C* are covered with Wratten *A*, *B*, and *C* filters such as are used in three-color work. The three groups of bars in the center are also covered, respectively, with these three filters. Originally it was the intention that each one of the three sections be provided with a neutral filter in addition to the colored filter. These neutral filters were to be so chosen that the three portions, when equally illuminated, would register as equally dense images on the negative made with the lens to be tested. Although such a balancing of the neutral filters can be obtained for a given box of panchromatic plates, it was soon discovered that the spectral sensitivity may vary so greatly with plates from different lots of emulsion that a readjustment of the filters would be desirable for each variation. To obviate this difficulty the neutral filters were removed and compensations secured by the sectored wheels shown in figure 4. Each sector disk is provided with three apertures which can be varied independently in angular width. The three apertures, instead of being left clear, are covered respectively with *A*, *B*, and *C* gelatine filters. Only the sector aperture covered with the *A* filter transmits light which is also transmitted by the *A* portion of the chart, and analogous statements are valid for the *B* and *C* parts of the chart. Consequently, the light transmitted by the three parts of the chart can be varied independently by the three apertures in the single sectored disk. This makes it a simple matter to adjust the three parts of the chart to register on the negative with the same amount of blackening. When investigating the chromatic aberrations as indicated by a negative obtained by this test it is necessary to make suitable allowance for the chromatic aberrations of the collimator objectives.

V. ADJUSTMENT OF INSTRUMENT

Four major adjustments must be correctly made in order that the results obtained may be satisfactory. The collimators must be focused so that the emergent rays are parallel; the angles between the axes of the collimators must have the desired values; the camera back

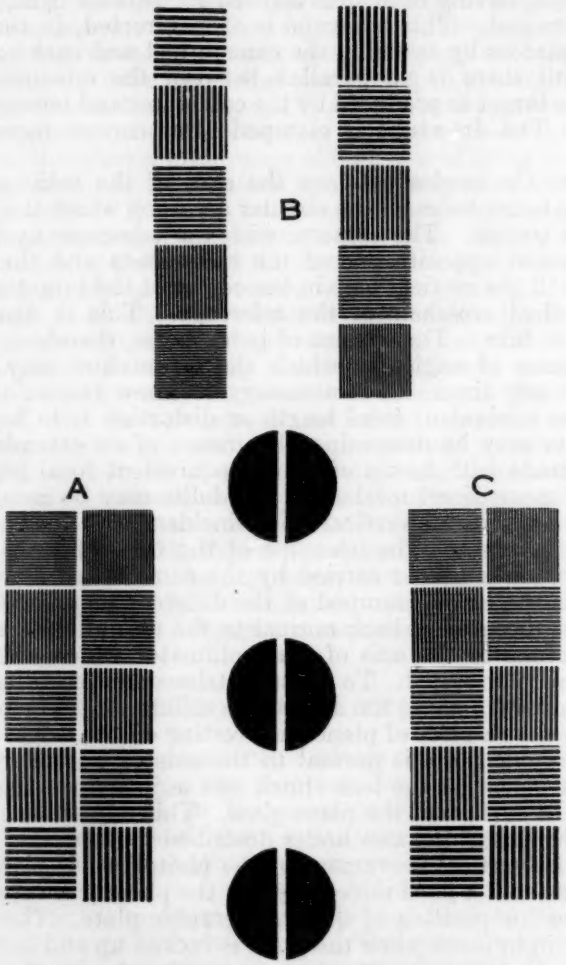

FIGURE 7.—*Chart for tests of chromatic aberration.*

The parts of the chart marked *A*, *B*, and *C* are covered, respectively with Eastman's *A*, *B*, and *C* filters. The circular disks in the center are similarly covered with the three different filters. The vertical marks in the disks serve as the fiducial marks for the determination of focal length and distortion for the different colors.

must be normal to the axis of the lens; and the plate must be translated in its own plane when it is shifted to present a fresh portion of its surface for each exposure.

To focus the collimators a telescope objective having a focal length of approximately 800 mm is placed in the chuck that ordinarily holds the lens to be tested. The carriage that carries the plateholder is

removed and a Gaussian eyepiece with crosshairs is mounted on the carriage that ordinarily carries the microscope. The eyepiece and telescope objective form a telescopic system. A silvered optical plane is placed in front of the telescope objective and, by means of the Gaussian eyepiece, the system is focused by autocollimation until the image of the crosshairs is superposed upon the crosshairs without parallax. The telescope, having been thus focused for parallel light, the optical plane is removed. This telescope is then directed, in turn, at each of the collimators by swinging the camera bed and each collimator is focused until there is no parallax between the crosshairs and the image of the target as produced by the collimator and telescope systems combined. The drawtube is clamped after correct focus has been obtained.

To adjust the angles between the axes of the collimators use is made of the index holes on the circular arc upon which the rear end of the camera travels. The camera, with the telescopic system still in place, is locked opposite one of the collimators and the collimator adjusted until the vertical bars in the center of the target are bisected by the vertical crosshair of the telescope. This is done for each collimator in turn. The system of index holes, therefore, provides a standard series of angles to which the collimators may be readily adjusted at any time. It is necessary to know the values of these angles if the equivalent focal length or distortion is to be measured. These angles may be determined by means of an extended series of exposures made with lenses of known equivalent focal length. In a second and more direct method, a theodolite may be mounted above the camera bed with its vertical axis coincident with that about which the camera revolves. The telescope of the theodolite may be autocollimated upon a mirror carried by the camera bed and the angles measured as the bed is clamped at the different index holes.

To adjust the camera back normal to the axis of the lens it is first adjusted normal to the axis of that collimator which will be coaxial with the lens to be tested. To do this a telescope with autocollimating eyepiece is directed along the axis of the collimator. The back is then adjusted so that a piece of plane glass resting on the ledges that locate the photographic plate is normal to the axis of this telescope. The lens is then placed in the lens chuck and adjusted so that its axis is normal to the surface of the plane glass. This adjustment of the lens is effected by use of the axis finder described by Bennett.[4]

To test the vertical movement of the photographic plate it is only necessary to focus a fixed microscope on the plane piece of glass which still occupies the position of the photographic plate. The glass plate should remain in focus when the plate is racked up and down.

VI. OPERATION OF LENS-TESTING CAMERA

After the instrument has been adjusted and the lens is properly aligned by means of the axis finder the exposures are made. If a new type of lens is to be tested the vignetting of the lens must first be measured. To do this the camera back is set at the best focus, as determined visually, and the apertures of the seven sectored disks are all set at the same opening. Without varying the focus a series of exposures are made with the duration of exposure increasing geo-

[4] BS Sci. Pap. 19, 587 (1924) S494.

metrically throughout the series. A 4 by 10 plate, as previously stated, permits 19 exposures to be made. By noting the exposures in the different columns that yield the same density a measure of the vignetting of the lens is obtained.

Next, the apertures of the sectors, on the basis of this measurement, are so adjusted that a given length of exposure will give the same blackening of the image in all columns. A suitable index plate for the detent mechanism on the micrometer-screw focusing movement is then selected to give the proper advance of the plate between exposures. The amount of the advance desired depends upon the relative aperture at which the lens is to be tested. If the relative aperture is f/4.5 an advance not greater than 0.05 mm per exposure is selected. With 19 exposures to the plate a total range of 0.90 mm of focus is explored on a single negative. If the relative aperture is smaller the advance is increased because of the greater depth of focus, this depth varying as the reciprocal square of the relative aperture. Before making the exposure the initial position of the camera back is so chosen that the central exposure of the range occurs when the plate is in the position of best focus. If all steps have been correctly taken the final negative will have seven columns of images of equal density, thus facilitating the judgment of the resolving power for different portions of the field. A horizontal row of images near the center of the range will be in best focus, with the rows above and below decreasing in sharpness.

To test a complete camera it is only necessary to remove the lens chuck and camera back of the apparatus and mount the airplane camera on a slide on the camera bed with the entrance pupil of the lens approximately at the intersection of the collimator axes and with the axis of the lens coaxial with that of the extreme right or left collimator. It is preferable to make two exposures, one with the right collimator coaxial with the lens, the second with the left coaxial. By this procedure a single row of images is recorded for an entire diameter of the field.

VII. PHOTOGRAPHIC TECHNIQUE

Eastman type *V–B* spectroscopic plates are used. This emulsion is much too slow for airplane mapping, but the resolving power is very much greater than for the usual panchromatic plate. This is an advantage for a test of lenses as it gives the lens an opportunity to show better resolution than can be recorded when used in the field. This makes it probable that an indicated deficiency of a lens, as shown by our tests, arises from a limiting fault in the lens rather than in the photographic technique. The plates are developed in developer prepared according to Eastman's formula *D19*, and they are fixed in solution *F5*.

VIII. INTERPRETATION OF TEST NEGATIVES

The arrangement of images on the resultant test negative is shown in figure 2. The negative is examined by means of a microscope to determine which row of exposures gives the best average definition across the entire field. After the most favorable row of images has been selected, the images in this row are carefully examined and the quality of definition is indicated by stating the number of lines per millimeter that is resolved at the different distances from the center

of the field. For each image two values are given, one applying to lines perpendicular to a radius drawn from the center of the field, the other to lines parallel to the radius. These values are designated respectively as tangential and radial resolving powers. Figure 8 gives enlarged reproductions of the images at the distance of best focus for a lens which covers a very large field with excellent definition. The resolving powers that are read from the negative are given in table 1.

TABLE 1.—*Resolving power of lens of figure 8*

	Degrees								
	0	5	10	15	20	25	30	35	40
Tangential	56	56	40	28	20	28	14	14	14
Radial	56	56	56	40	40	40	40	20	*

* The resolution here is less than that corresponding to the coarsest pattern on the chart, namely, 3.5 lines to the millimeter.

For the series of reproductions in figure 8 the key diagram at the left indicates the number of lines to the millimeter in each pattern of the target.

After the best horizontal row of images has been selected one counts up to this row from the last exposure and, knowing how much the plate was advanced between each two exposures, and having measured the distance from the vertex of the last surface of the lens to the emulsion when in position for the final exposure, one readily determines the back focal length corresponding to the position of the plate that yielded the best definition. In determining the back focal length in this manner the precision is limited by the precision with which one can select a given horizontal row on the test negative as representing the best average definition. The back focal length is not a uniquely determined quantity but there is a range of values corresponding to the depth of focus. This range of values over which the definition appears to have no significant difference in quality arises from the limited resolving power of the lens, the presence of aberrations and the granular character of the photographic emulsion. The larger the relative aperture of the lens the less will be the depth of focus. When a lens is tested with the diaphragm set at f/4.5 it is customary to advance the plate 0.05 mm between exposures, and there are usually at least three adjacent rows on the plate that present excellent images and differ from each other only slightly in average excellence of imagery. When a lens is tested at f/11 the movement of the plate between exposures is seldom less than 0.10 mm. Consequently, the back focal length is usually determined with an uncertainty of the order of ± 0.05 mm and our reports, in such cases, make no estimate of the probable error other than the statement that it does not exceed ± 0.10 mm. This uncertainty causes the user of the lens no difficulty because it arises from no defect in the testing or in the camera but rather from an inherent or essential lack of precision with which the back focal plane can be experimentally located.

After the back focal length has been determined for the row of best definition the distances from the vertical bar of the axial images to

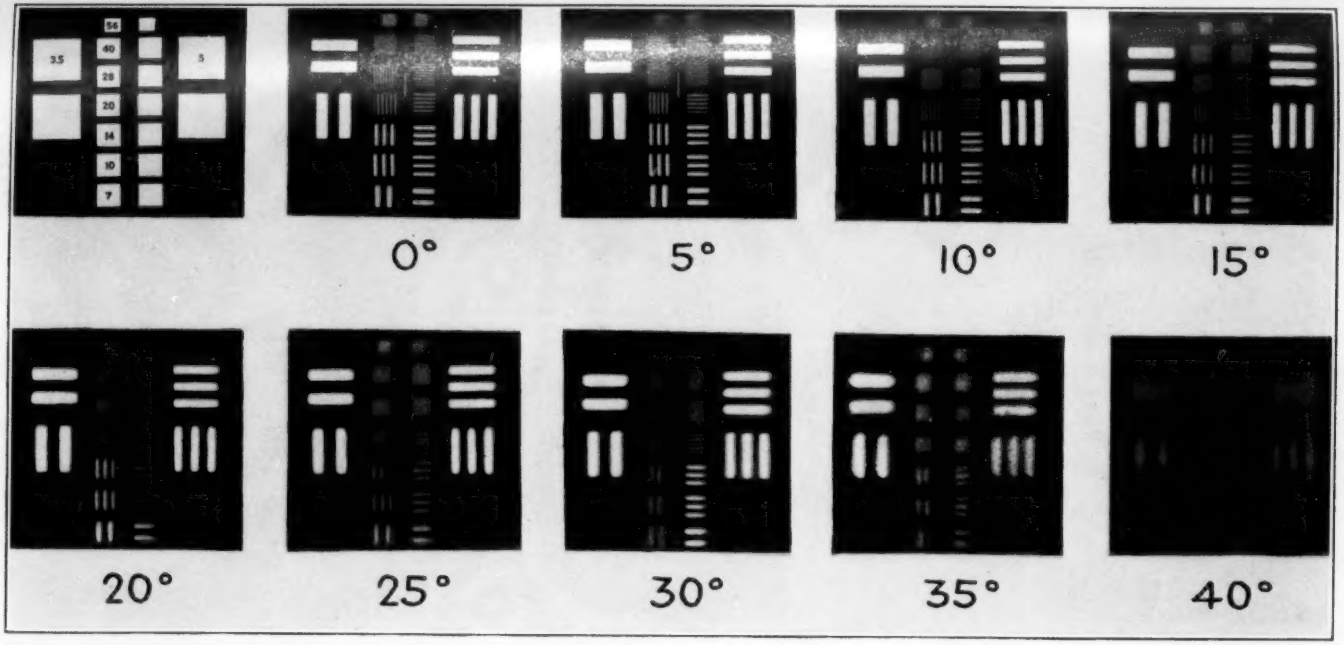

FIGURE 8.—*Test of definition.*

The standard test chart has been photographed at five-degree intervals from center to edge of the field and the resulting images enlarged approximately 12 diameters. The resolving power can be found by referring to the key diagram (upper left), which gives the number of lines per millimeter on the negative corresponding to any element of the target. These reproductions demonstrate the excellent performance of a wide-angle lens, focal length 6½ inches, aperture f/11, specially designed for photogrammetric work although they fail to record the finest detail of the original negative. The resolving powers, as read from the negative, are tabulated on page 458.

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the corresponding bar in each of the other images in the same horizontal row is measured on the test negative. If there were no distortion, any one of these distances, divided by the tangent of the angle between the two corresponding collimators, would give the equivalent focal length. In general, because of the presence of distortion, the quotients obtained for the different angular distances will vary. In such cases it is customary to assume that the distortion for the images 5 and 10° from the axis is negligible and obtain two determinations of the equivalent focal length from these two images. If this assumption is justifiable the two values of the equivalent focal length will agree closely and the mean is adopted as the equivalent focal length.

The probable error in the determination of the equivalent focal length depends upon the probable errors in the measurement of the angles between the collimators and the distances between the images on the test negatives. The angle between any two collimators can be determined with a probable error that does not exceed ± 7 seconds and the lengths on the negative with a probable error that does not exceed ± 5 mμ. These values do not represent the probable errors obtained when a series of readings is made in rapid succession and averaged but may be termed effective probable errors and are made large to include the variations arising from inexact mounting of the lens in the lens chuck, secular changes of the apparatus and other causes that remain relatively constant during the progress of a given test but may change from test to test.

Applying these effective probable errors, the determination of equivalent focal length based upon the image 5° from the axis has a probable error of approximately ± 0.1 mm and, for the 10° image, the corresponding probable error is approximately half this. Consequently, the probable error in the determinations of the equivalent focal length does not exceed ± 0.1 mm.

The distance from the central image to any image at an angular distance θ from the axis, minus the product of the equivalent focal length by $\tan \theta$, gives the distortion for the angular distance θ from the axis. This represents the actual displacement of the image from its distortion-free position, a positive value indicating that the image is displaced from the center of the picture outward as a result of the distortion. The determination of distortion, therefore, is based upon measurements precisely similar to those required for the determination of the equivalent focal length and subject to the same probable errors. The probable error in the determination of distortion is approximately proportional to the distance of the image point from the center of the field. Using the effective probable errors that have been given, the probable error for a point 115 mm from the center of the field (the center of one side of a 9- by 9-inch negative) does not exceed 0.02 mm for lenses of 150- to 200-mm focal length. In all of the foregoing measurements it is believed that the systematic errors of the testing camera fall within limits not exceeding the probable errors that have been given.

The equivalent focal length and distortion obtained by these procedures are the values as customarily defined for the purposes of geometrical optics. Actually the photogrammetist uses the equivalent focal length as a scale factor for the reduction of measurements made on his negatives. The presence of distortion indicates that the true scale factor varies from one part of the negative to another

The value of the equivalent focal length, as referred to in the preceding paragraphs, is the scale factor for the central portion of the negative only. If the distortion is measured at 5° intervals from the center to the edge of the field it may be possible to adopt a scale factor corresponding to some other portion of the negative and secure a better average fit over the entire field. This is an advantageous procedure with a lens having a large amount of distortion. Usually, however, the better quality airplane camera lenses that are now being submitted have so little distortion that this seems an unnecessary refinement. It is not uncommon to have the distortion at 30° from the axis as small as 0.03 mm even when no such adjustment of the equivalent focal length has been made.

When a complete camera is received for test it has usually been focused and the lens and the guides locating the plane occupied by the film are adjusted and locked in the relative positions that they will have when the camera is used in the field. Consequently, the choice of back focal length has already been made and, if its value is required, it is only necessary to make a measurement, by means of a depth gage or other convenient instrument, of the distance from rear vertex of lens to the plane occupied by the photographic emulsion.[5]

As has been previously mentioned, an exposure with a camera yields a single row of images corresponding to the row of images giving the best average focus on a test negative made when testing a lens. These images are examined for a determination of resolving power and the distances between the vertical bars of the images are measured, after which the equivalent focal length and distortion are determined in the manner already described.

WASHINGTON, January 11, 1937.

[5] If the camera contains a glass pressure plate between the photographic film and the lens this measured distance should be decreased by one-third the thickness of the pressure plate.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP985

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BOILING-POINT–COMPOSITION DIAGRAM OF THE SYSTEM DIOXANE-WATER

By Edgar R. Smith and Mieczysław Wojciechowski [1]

ABSTRACT

Dioxane and water form a positive homoazeotrope which has an azeotropic decrease in temperature sufficiently large to effect the complete removal, by fractional distillation through an efficient column, of water present as an impurity. The boiling-point–composition diagram, including the composition of the vapor in equilibrium with the boiling liquid, was determined. The normal boiling point of dioxane was found to be 101.320° C.

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I. INTRODUCTION

During the past few years, the system dioxane (1,4-diethylene dioxide)-water has received considerable attention, for several reasons. The boiling point, freezing point, and density of dioxane are not very different from those of water and, what might be least expected considering its symmetrical ether structure and nonpolar character, it is miscible with water in all proportions. These mixtures are of particular interest in electrochemistry because the low dielectric constant of dioxane permits the preparation of a mixture having any desired dielectric constant between the values of about 2 and 80. Åkerlöf and Short [1] [2] measured the dielectric constants of dioxane-water mixtures over the temperature range 0 to 80° C. Kraus and Fuoss [9] used mixtures of dioxane and water in a study of the conductance of electrolytes as influenced by the dielectric constant of the solvent medium. Grady [6] measured the infrared absorption spectra of this system. From a study of the freezing points of solutions of normal water and of deuterium oxide in dioxane, Bell and Wolfenden [3] were able to show that the association factor for D_2O is about 3 percent more than for H_2O at the same concentrations. Gillis and Delaunois [5] measured the freezing points, boiling points, densities, and indices of refraction of the system water-dioxane. Their measurements of boiling point, however, were reported only to 0.1° C and were not corrected to normal pressure. They made no attempt to establish the composition of the vapor phase in equilibrium with the boiling

[1] Guest worker from the Polytechnic Institute, Warsaw, Poland.
[2] The figures in brackets here and throughout the text refer to the references at the end of the paper.

liquid for any point of the system. Hovorka, Schaefer and Dreisbach [8] measured densities, surface tensions, and total vapor pressures in the system from 10 to 80° C and, in addition, the partial vapor pressures and indices of refraction at 25° C, and the freezing points. Geddes [4] measured the fluidity of dioxane-water mixtures over the whole range of composition between 20 C and 80° C. Scatchard and Benedict [12] measured the freezing points of dilute solutions of dioxane in water and the effect of added salts on the freezing points. Hertz and Lorentz [7] measured the densities, viscosities, surface tensions, and refractive indices of the system over the whole range of composition at several temperatures.

In the present investigation the boiling-point–composition diagram at normal pressure for the system dioxane-water was determined over the complete range of composition.

II. MATERIALS AND APPARATUS

Three kilograms of the best grade of 1,4-dioxane sold by the Eastman Kodak Co. was distilled through a vacuum-jacketed, 40-bulb, glass rectifying column [15] equivalent to about 30 theoretical plates. Dioxane and water form a positive homoazeotrope (homogeneous mixture of minimum boiling point) which contains about 52 mole percent of water. The boiling point of this azeotrope (87.82° C) is so much lower than the boiling point of dioxane (101.32° C) that water, if present in not too large an amount, can be removed completely in the head portions of a fractional distillation, thus permitting the collection of anhydrous dioxane in the middle and tail fractions. The anhydrous dioxane prepared in this way was found to be of a high degree of purity when tested in a standard differential ebulliometer [15].

The water used for preparing the mixtures of dioxane and water, and for the comparative standard for the boiling-point determinations, was prepared by redistillation with alkaline permanganate of the distilled water supplied to the laboratory, following this by a simple distillation, rejecting the first and last portions in each case.

For the determination of the boiling points two ebulliometers were used. One of these was a simple barometric ebulliometer containing the redistilled water for the reference standard. The other was a standard differential ebulliometer containing the dioxane or the mixtures of dioxane and water under investigation. These ebulliometers, together with their accessories, have been described in connection with the determination of the boiling-point–composition diagram for dilute aqueous solutions of deuterium oxide [13]. The same platinum-resistance thermometer and Mueller thermometer bridge were used in this investigation.

III. PROCEDURE AND RESULTS

First, the boiling point of dioxane of a known degree of purity was determined. To remove moisture absorbed by the hygroscopic dioxane during its transfer to the ebulliometer, several portions of 2 to 3 ml were distilled from the side tube of the condenser.[3] After this was done, the difference between the boiling point and condensation temperature, Δt, was only 0.003° C, which corresponds to the fifth or highest degree on the Świętosławski scale of purity [15]. The boiling point was next determined at the prevailing atmospheric pressure and

[3] Reference [13] figure 2.

at two other pressures, one slightly below and one slightly above 1 atmosphere. By this procedure the value of the change in boiling point of the dioxane, Δt_s, and the change in boiling point of water, Δt_w, corresponding to the same change in pressure were obtained at pressures slightly above and slightly below 1 atmosphere. The ratio $\Delta t_s/\Delta t_w$ at 1 atmosphere was then computed and the normal boiling point of the preparation was calculated by the formula [16] $t_s=t'_s+(100-t'_w)\Delta t_s/\Delta t_w$, in which t_s is the normal boiling point of the preparation under investigation and t'_s and t'_w are the boiling points of the preparation and of water, respectively, measured under the same actual pressure. The normal boiling point thus obtained for this sample was 101.321° C. The boiling point found for a second fraction of the dioxane, having $\Delta t=0.004°$, was 101.319° C.

A series of mixtures of dioxane and water were prepared, and the values of their normal boiling points and of the differences between their boiling points and the temperatures of condensation of their vapors were measured in the differential ebulliometer, using the same procedure. It was shown in a previous investigation [13] that the amount of fractionation which occurs in this differential ebulliometer is very nearly equivalent to that of one theoretical plate of a fractionating column. With this knowledge it is a simple matter to construct the vapor-composition curve as well as the liquid-composition curve from the boiling point and Δt data. However, over most of the range the vapor has a composition considerably different from the liquid, and the composition of the latter is thereby altered from its original value, since the amount of the vaporized mixture in the dead space above the boiling liquid is appreciable. To make the necessary correction, the volume of the dead space and the amount of condensed vapor in the drop counters and upper boiling tube were determined roughly. Then from a preliminary boiling-point–composition diagram, in which the original compositions were plotted as abscissa, the compositions of the vapor phase were determined for each mixture with sufficient accuracy to make the required small correction to the liquid compositions.

TABLE 1.—*Data for the boiling-point–composition diagram*

Mole percent dioxane (corr.)	Boiling point	Δt	Condensation temperature	$\Delta t_s/\Delta t_w$	$\Delta t_s/\Delta p$
	°C	°C	°C		°C/mm
0.00	100.000	0.000	100.000	1.000	0.03685
2.12	97.29	7.09	90.20	0.992	.0366
4.42	94.00	5.06	88.94	.975	.0359
7.33	91.97	3.62	88.35	.980	.0361
11.33	90.52	2.43	88.09	.984	.0363
15.76	89.41	1.53	87.88	.988	.0364
24.44	88.44	0.599	87.84	.993	.0366
32.44	88.04	.244	87.80	.998	.0368
37.41	87.90	.114	87.79		
43.54	87.84	.059	87.78	1.000	.0369
45.27	87.83	.047	87.78	1.002	.0369
46.91	87.82	.039	87.78		
57.55	87.95	.124	87.83	1.010	.0372
67.77	88.44	.444	88.00	1.021	.0376
79.99	90.09	1.17	88.92	1.055	.0389
87.96	92.70	2.89	89.81	1.122	.0414
95.75	97.24	3.01	94.23		
100.00	101.320	0.003	101.317	1.173	.0432

The data obtained are given in table 1. The first column contains the corrected mole percentage of dioxane in the liquid phase, the second the normal boiling point of the liquid, the third the difference between the boiling point of the liquid and the condensation temperature of the vapor, the fourth the condensation temperature (boiling point $-\Delta t$), the fifth the value of the ratio $\Delta t_s/\Delta t_w$ at 1 atmosphere, and the sixth the value of $\Delta t_s/\Delta p$ at 1 atmosphere obtained by multiplying $\Delta t_s/\Delta t_w$ by the value of $\Delta t_w/\Delta p$, 0.03685°/mm [14].

The boiling-point–composition diagram for the system at 1 atmosphere is shown in figure 1. The composition of the positive homoazeotrope lies between 47 and 48 mole percent of dioxane. An interesting observation here, that has been noted previously for other systems [15], is that the degree of purity of the azeotrope, as indicated by its Δt, is markedly lower (third degree) than the purity of the components (fifth degree). This is due to the high sensitivity of the azeotropic mixture towards very small amounts of impurities, which seems to be a general phenomenon. It is also noteworthy that the boiling point of dioxane is very much lowered by a small amount of water. Thus, 1 percent of water by weight (4.7 mole percent) lowers the boiling point by 4°. Accordingly each 0.001° lowering corresponds to 0.00025 percent by weight of water. A comparison of the values for the normal boiling point of dioxane obtained by different investigators is shown in table 2.

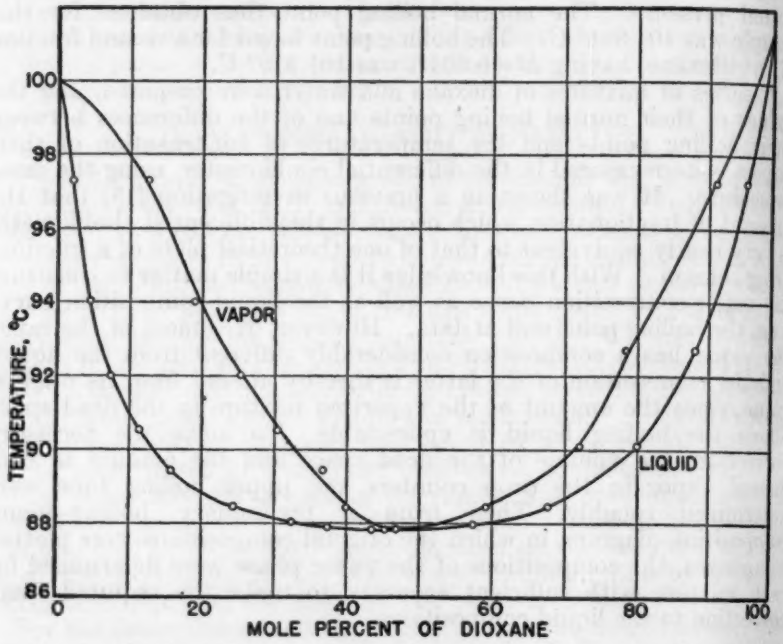

FIGURE 1.—*Boiling-point–composition diagram for the system dioxane-water.*

TABLE 2.—*Boiling point of dioxane*

Observer	Normal boiling point	$(dt/dp)_{760mm}$
	°C	° C/mm
Anschütz and Broeker [2]	101.2 to 101.4	
Gillis and Delaunois [5]	101.4	
Hertz and Lorentz [7]	100.2 to 100.4	
Kraus and Vingee [10]	[1] 101.24	
Milone [11]	100.7	
Scatchard and Benedict [12]	101.22	
Smith and Wojciechowski	101.32_0	0.0432

[1] At 761 mm.

On standing at room temperature in a bottle having its ground-glass stopper covered by a paraffin-sealed hood to prevent contamination, dioxane was found to undergo a slow change, probably a polymerization, which increases its boiling point. One sample, after standing in this way for 12 weeks, had a normal boiling point of 101.44° C, the increase amounting on the average to about 0.01° per week. The value of $\triangle t$ for this sample was 0.094°. To obtain accurate measurements on dioxane it is, therefore, necessary to use freshly purified samples as well as to take precautions to exclude moisture.

One of us [4] wishes to express gratitude to the Polish Fundusz Kultury Narodowej in Warsaw for financial aid.

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WASHINGTON, January 15, 1937.

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RESEARCH PAPER RP986

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"CAMERA FINISH" AT THE RACE TRACK

By Irvine C. Gardner

ABSTRACT

Cameras have been generally installed at race tracks to automatically photograph the finishes of the races. If a race is too close to permit placing the horses by visual observation the judges may use photographs as a basis for their decision. There has been considerable criticism of the camera, and some have questioned the accuracy of the pictures that are obtained. A discussion of possible sources of errors and a quantitative appraisal of their importance are given. The conclusion is that relatively simple precautions make the camera a reliable instrument for determining the outcome of a race. In installations that have been examined these precautions have received adequate attention.

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I. INTRODUCTION

It is not unusual for the finish of a race to be so close that the judges are unable to agree upon the order in which the horses should be placed. To meet this difficulty recourse has been made to the use of cameras which automatically photograph the finish of the race and which provide photographs upon which the judges may base their decisions. This procedure has been so generally adopted that substantially all race tracks are equipped with camera installations, and their use has resulted in the coinage of the newspaper expression "camera finish" and "photo finish" to designate a finish so close that the judges are unable to reach a decision without an appeal to the photographic evidence.

This universal installation of photographic equipment at the tracks should not be understood to imply that their introduction has met with the general approval of followers of the races. On the contrary, many decisions based upon the camera have been caustically criticized, and these criticisms have been given coherence by the newspapers, which have printed many comments intended to indicate that the cameras, for some reason not detailed, favor the outside horse, that is, the horse farthest from the rail. As a result, a curious situation has developed.

The judges on the one hand, although most favorably situated to view the finish of a race, readily admit their inability to place the horses with certainty in a particularly close heat and voluntarily appeal to the camera for assistance. On the other hand, the spectators, less favorably situated than the judges, do not hesitate to affirm their ability to correctly place the horses by visual observation and, on the basis of their decision, accuse the camera of inaccuracy. As a consequence, the New York State Racing Commission has asked the National Bureau of Standards to investigate the installations at the different New York tracks. In view of the considerable interest in the decisions of the camera, as evidenced by the frequency of comment in the daily newspapers, it has been considered desirable to set forth the conditions necessary for the correct photographic representation of the finish of a race and also to estimate, quantitatively, the errors which may result from the neglect of certain precautions.

Before proceeding with the consideration of these conditions governing accuracy of performance, it is advisable to set forth the restrictions governing the choice of material for this presentation. There are many factors that determine the desirability of a given type of camera installation. Important requirements are certainty of operation, rapidity of operation, and accuracy of representation of the finish. Of these, the first two depend upon such details as the type of photoelectric cell unit employed to actuate the camera, the excellence of design and workmanship of the mechanical parts, the presence or absence of automatic apparatus for developing the film, the enlarging apparatus, and other features of construction. As the present-day camera installations are far from standardized in construction or operation, no important general conclusions regarding certainty and rapidity of operation can arise from a consideration of installations at a few tracks. Each installation must be examined and judged upon its merits. All of the installations, however, have the principle in common that the accuracy of a photograph of the finish depends upon the operation of a lens and shutter, elements for which considerable standardization already exists. Examination of a few installations, therefore, readily leads to conclusions which in these respects, are valid for all. Consequently, this paper will be definitely restricted to a consideration of the factors that govern the production of photographs that will correctly represent the finish of a race.

The factors which may cause a photograph to be incorrect or misleading are: (1) action of the shutter; (2) relative position of camera and finish line; and (3) perspective.

II. ACTION OF THE SHUTTER

1. SINGLE-EXPOSURE CAMERA

In the single-exposure or "still" camera a focal-plane shutter is commonly employed. With this type of shutter the exposure is made through a narrow slit which rapidly travels across the plate. It follows that the entire picture is not taken at the same time but that different parts of the film are successively exposed. In a typical focal-plane shutter as used for fast moving objects, the width of the travelling slit is ⅛ inch. If the exposure is $\frac{1}{100}$ second the slit travels at a rate of 62.5 inches per second. If the direction of travel of the slit is parallel to the longer side of a 4 by 5 plate, one edge exposed 0.08 second later than the opposite edge. It is importan

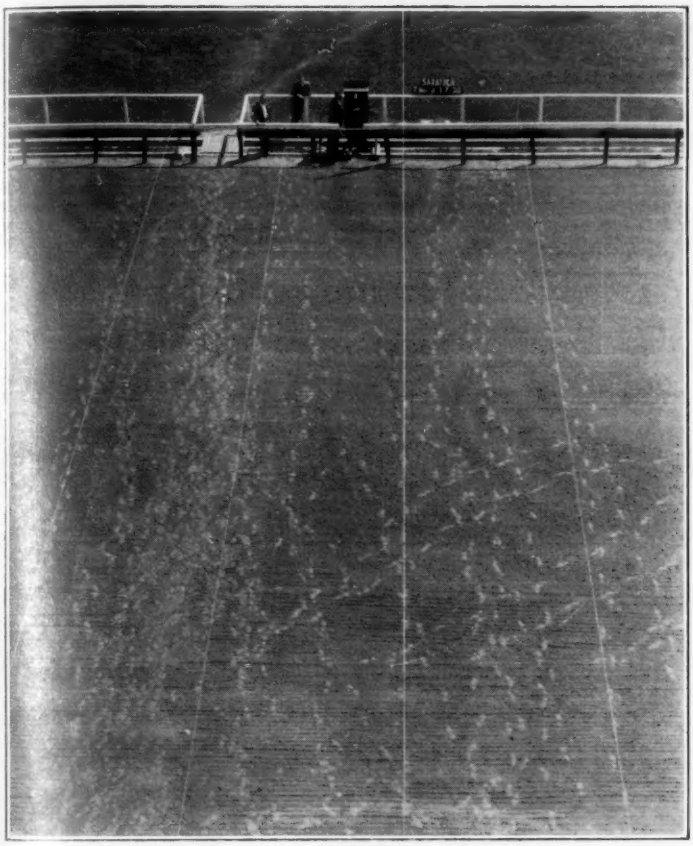

FIGURE 1.—*A photograph of the track at Saratoga Springs made with one of the recording cameras.*

The vertical white line is the finish line under which the horses pass. The three lighter lines are cords temporarily stretched, for this photograph, parallel to the finish line and spaced 10 feet apart. The convergence of these lines is illustrative of the extent to which parallel lines are rendered convergent by perspective. The enlargement of a finish, as prepared for the judges, shows only a small area of this photograph, next to the rail, enlarged approximately 5 diameters.

FIGURE 3.—*A reproduction of a portion of the photograph of the finish of the eleventh race on August 17, 1936, at Saratoga Springs.*

The outside horse, Jaber, numbered 6, was judged to be the winner. The newspapers, in criticizing this decision, stated that the spectators generally believed that Captain Jinks, the horse nearer the rail, should have been declared the winner. Analysis indicates that the photograph must have placed the two horses correctly in this race.

therefore, that the direction of travel of the shutter be such that this difference in time will introduce no error. For correct results the direction of travel must be such that the entire finish line is photographed at the same instant. This is generally understood, and it is believed that this rule is followed at all camera installations.

Nevertheless, since the use of a vertically moving shutter has been often considered, it is interesting to determine, quantitatively, the errors which might result from a violation of this principle. Figure 1 is an actual photograph made at the Saratoga Springs track with the regular camera installation. Three lines were stretched across the track, parallel to the finish line and spaced 10 feet apart. These lines afford a convenient scale for the interpretation of the photograph and also show, by their convergence, the result of perspective. Figure 2 is a tracing of the essential parts of this photograph, inverted because this is the way the image appears on the ground glass. It will be assumed that two horses are running a dead heat with their noses at the finish line at X and Y. These positions have been selected to correspond to points approximately 5 and 15 feet from the rail. (It will be understood that this photograph shows a large width of the track which is never used at the time of the finish of a race. Actually, the competing horses in a near dead heat will often be crowded together and the leaders are seldom laterally separated as much as 10 feet, measured along the finish line.) The horizontal slit of the focal-plane shutter is shown at AB in a position to photograph Y, the outside horse. The horse X, nearer the rail, will not be photographed until the slit has travelled downward a distance of approximately ¾ inch on the film. With the slit travelling 62.5 inches per second this corresponds to a time interval of 0.012 second, during which the horse, travelling at an average speed of 55 feet per second, will have advanced 0.66 foot or approximately 8 inches. Consequently, in a dead heat, with this arrangement, the horse next to the rail will be favored, and he will be given a spurious lead of 8 inches.

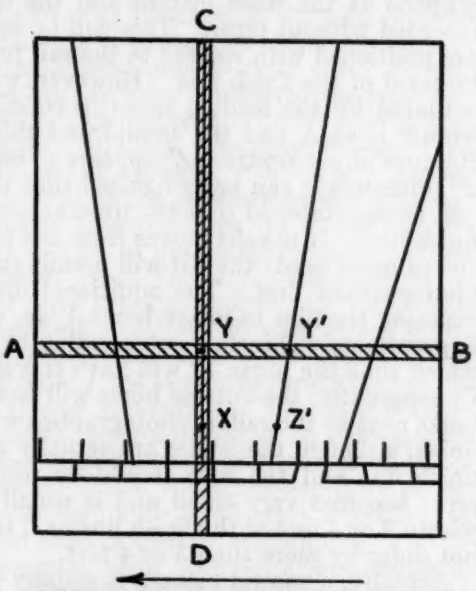

FIGURE 2.—*A tracing of the essential portions of figure 1, inverted to bring it into its position as imaged on the ground glass of the camera.*

As a result of the inversion the direction of travel of the horses is from right to left on this page. *AB* represents one position of the slit of a focal-plane shutter for which the slit travels in a vertical direction. *CD*, similarly represents the slit of a focal-plane shutter for which the slit travels horizontally. This illustration is reduced to about one-half. Measurements given in the text were made on original 4- by 5-in. negative.

In considering this result it should be noted that the values have been consistently chosen to yield a large error. Actually, the exposure will probably be 0.001 second, in which case the shutter speed

The outside horse, Jaber, numbered 6, was judged to be the winner. The newspapers, in criticizing this decision, stated that the spectators generally believed that Captain Jinks, the horse nearer the rail, should have been declared the winner. Analysis indicates that the photograph must have placed the two horses correctly in this race.

is doubled. Also the two horses running the dead heat may have crowded as close to the rail as possible so that they are 5 feet instead of 10 feet apart (measured along the finish line). In such a case the error resulting from this worst possible installation of the focal-plane shutter will be 2 inches. If the vertically travelling focal-plane shutter moves upward instead of downward the outside horse will be favored but the amount of the error remains the same.

Greater interest is attached to the focal-plane shutter as commonly installed with a vertical slit travelling horizontally. In figure 2, *CD* indicates such a vertical slit assumed to be travelling from left to right. This is the usual direction of travel. The entire finish line is photographed at the same instant and the dead heat or a close finish is recorded without error. This will be so, no matter where the horses are positioned with respect to the rail provided they are in the neighborhood of the finish line. However, with a single-exposure camera, actuated by the leading horse, a condition may arise in which the winner is at X and the second and third horses are at Y' and Z'. Because of perspective, Z' appears to be nearer the finish line than is Y', although it can be recognized that they are actually even since it will be remembered that the lines across the track are parallel to the finish line. If the slit moves from left to right (the usual direction in the cameras used) the slit will permit the horse next to the rail to be photographed first. The additional distance the slit travels before exposing the film to image horse Y' is, with the horses 10 feet apart, approximately ⅛ inch, corresponding to a lag of 0.002 second, during which time the horse Y' will have travelled approximately 1¼ inches. Consequently, the outside horse will be shown 1¼ inches ahead of the horse next to the rail, if photographed when both are 10 feet from the finish, although the horses are actually at the same distance from the finish line and the race should be recorded as a dead heat. This error becomes very small and is usually negligible if the horses are within 2 or 3 feet of the finish line or if their distances from the rail do not differ by more than 3 or 4 feet.

Actually, a second camera is usually provided and, in the example that has been considered, a second photograph would have been made with the horses Y' and Z' at the finish line. This procedure should always be followed as, otherwise, the horses Y' and Z' are photographed before they have completed the race, and their relative positions may change during the remaining few feet which they are to run.

Even when the second camera is provided, however, in general, it will not function unless there is no overlapping between the leading horse and the next two. Consequently, cases may occur in practice when second and third places will have to be awarded on the basis of a picture which shows the horses nearly a length from the finish line. If the horses Y' and Z' in such a case are assumed to be not more than 8 feet from the finish line and are separated laterally by a distance of 10 feet, this will introduce an error of approximately 1 inch in the relative positions of the two horses. Usually the lateral spacing is much less than 10 feet and the horses will be less than 8 feet from the finish line and the error correspondingly reduced.

2. MOTION-PICTURE CAMERA

The motion-picture-camera shutter is a rotating disk with a radial aperture. This is mounted back of the lens and, because of the short focal length, it cannot be far from the focal plane. Consequently, the shutter acts in a manner intermediate between that of the between-the-lens shutter and the focal-plane shutter. The opening in the rotating disk is so large that the entire frame is simultaneously exposed during a part of the exposure, but the exposure begins at one edge of the frame and ends at the opposite edge. The ordinary motion-picture camera takes 20 pictures per second and approximately half the time is required for advancing the film between exposures. Consequently, the over-all duration of a single exposure is 0.025 second, and the instants of exposure for different parts of the frame cannot differ by an amount greater than this. For the 4 by 5 focal-plane shutter that has just been considered the analogous difference in time is 0.08 second. Therefore, the errors arising from nonsimultaneous exposure of the film are less than one-third the corresponding errors for the single-exposure camera. A camera operating at normal speed, however, is not satisfactory in the present case because the horses advance approximately 30 inches between exposures, and one cannot be certain of obtaining pictures with the horses sufficiently near the finish line. Therefore, the speed of the camera is stepped up to two or three times normal and all of the errors are further reduced to a negligible value. Furthermore, in the consideration of the single-exposure camera, it will be recalled that considerable attention was given to the condition arising when the second and third horses are closely matched and less than a length behind the first. In such a case the judges must rely on a photograph showing the first horse at the finish line and the second and third horses at small distances from it. With the single-exposure camera this introduces a systematic although very small error in placing the second and third horses. This error is usually negligible. With the motion-picture camera this source of error does not arise because the camera operator may select, for enlargement, frames showing the second and third horses when at the finish line.

III. RELATIVE POSITION OF CAMERA AND FINISH LINE

The camera is mounted high above the track at the back of the stand, over a prolongation of the finish line. The finish line is 10 or 12 feet above the track and is supported at the end over the rail by an upright carefully guyed so that it is accurately vertical. The line and the upright determine a vertical plane extending across the track and the horses are placed in the order in which their noses come into this plane. The camera must be so positioned that this plane is photographed as a vertical line in the picture. It is not necessary to make an elaborate survey in order to determine the correct placing of a camera as each photograph of a race indicates whether or not the camera is correctly placed. On the photograph the image of the overhead finish line should be exactly superposed upon that of the upright. Close examination of the photograph from which figure 3 was copied will show that this condition is not exactly fulfilled, although the defect is quite insignificant in amount and may not be apparent in the reproduction.

IV. PERSPECTIVE

The four converging lines of figure 1 are representative of parallel lines on the track. The apparent convergence is not caused by a defect in the lens but is a necessary consequence of the placing of the camera. The photograph gives the appearance of the track as viewed from the camera booth in true perspective. This apparent displacement arising from perspective becomes greater at greater distances from the finish line, but at the finish line it is entirely absent.

If a single-exposure camera is employed, the interruption of the beam of light falling upon the photoelectric cell should cause the picture to be taken when the horse is at the finish line. Figure 3 is a sample photograph from the Saratoga Springs track, and is an excellent example of good timing of the instant of exposure. If the second and third horses are less than a length behind the first horse no exposure will be available showing them at the finish line. This case has already been discussed from the standpoint of errors which may be introduced into such a picture because of the use of a focal-plane shutter. But even if the picture is correctly made and free from error arising from the action of the shutter there is still the possibility of an incorrect decision because of the failure to allow for the effect of perspective. If, as before, it be assumed that one horse is 10 feet farther from the rail than another and that both are approximately 5 feet from the finish, the error from the neglect of perspective will be approximately 1 foot and in favor of the horse next to the rail. This has been determined by scaling the value from figure 2 and, therefore, applies only to the installation at Saratoga Springs, but errors of approximately the same magnitude may be expected at other tracks.

The allowance for perspective, however, can be easily and accurately made. As a preliminary step, stretched parallel strings a foot apart and at the average height of a horse's nose, on the side of the finish from which the horses approach, can be photographed with the camera in its regular position and the resulting negative enlarged to the same size, as is customary for the purposes of the judges. The pattern of lines, including the finish line, should then be reproduced on a piece of transparent celluloid and made available to the judges. In a doubtful case the celluloid should be placed over the photograph with the finish lines coinciding. A dead heat will be indicated if two horses have their noses on the same member of this family of converging lines.

As already mentioned, if an installation is equipped with a motion-picture camera, and the close decision is between the second and third horses, a frame should be selected for enlargement in which these two horses are at the finish line. This completely eliminates any inaccuracy of interpretation arising from perspective, and the possibility of selecting such a frame is one of the important advantages of the motion-picture camera installation.

V. CRITICISM OF CAMERA DECISIONS

It has already been pointed out that the criticism of camera decisions has been sufficiently general to gain frequent mention in the newspapers. A hypothesis has gradually evolved that the camera favors the outside horse. The photograph shown in figure 3 is a case in point. On the basis of this photograph the decision was

awarded to Jaber, horse 6. The camera was properly mounted with the focal-plane shutter travelling in a horizontal direction. The photograph itself contains evidence that the other conditions are satisfactorily complied with. The camera actuating device operated to take the picture when the horses were at the finish line. The photographs show exactly what the judges would have seen had they been situated above the finish line and had they been able to judge the rapidly moving horses with the accuracy of the camera. The following morning one of the more conservative news items regarding the decisions says:

> The first public dissatisfaction with the camera developed in the nightcap when the outside horse, Jaber, was shown as the winner, after Captain Jinks had appeared very definitely first to practically all unofficial observers.

It must be kept in mind that the camera is not used for all races. The photograph is requested only when the judges are unable to agree upon the winner. Therefore, the race was too close to be decided by the judges, although the spectators definitely believed that the inside horse had won. This unanimity of opinion forbids its dismissal as unimportant. Perhaps it can be explained by considering the positions of the spectators. At a race track they are grouped in two stands, one in advance of, the other beyond the finish line. The spectators in the stand on the approach side of the line are prevented from accurately judging the finish of a close race because they cannot see the horses' noses. Those in the stand beyond the finish line view the horses approaching the finish. Their line of sight necessarily cuts across the track at an angle with the finish line in such direction that the horse next to the rail is favored. Although this interpretation may not be susceptible of direct proof it presents a consistent picture. If the race is nearly even with the outside horse leading, the spectators erroneously place the inside horse ahead, because of the angularity of view, and the camera is credited with having favored the outside horse. On the other hand, if the inside horse is only slightly ahead, the spectators place him farther ahead and the camera loses credit for giving a close decision to the horse next to the rail. Consequently, the belief has developed that the camera favors the outside horse.

VI. CONCLUSION

A photograph of a finish contains, within itself, evidence sufficient to determine whether or not the camera was correctly placed and whether or not the exposure was made at the proper instant. If in the photograph the finish line superposes upon its supporting post and if the winning horse has his nose on the finish line there are no errors arising from the position of the camera or from perspective. If a motion-picture camera taking 60 or more pictures per second is used, or if one employs a single-exposure camera with its focal-plane shutter arranged to photograph simultaneously the entire finish line, then the picture is without error for all horses at the finish line. Figure 3 is a picture complying with these requirements, and it is decisions rendered on pictures of this nature that have given rise to adverse criticism, which careful examination shows to be without foundation.

If a motion-picture camera is employed, the frame showing the competing horses at the finish line should be selected for enlargement and transmission to the judges. If the close decision does not involve the first horse, this frame may show the winning horse beyond the finish line.

If a single-exposure camera is used and two competing horses are less than a length behind the first horse, a picture showing the competing horses at the finish will not be available. In such a case the focal-plane shutter, if it moves from left to right, as illustrated in figure 2, will slightly favor the outside horse. On the other hand, if perspective is neglected, there will be an error from this source favoring the horse next to the rail. The error from the shutter will probably not exceed 1 inch and does not affect the horse at the finish line. The error arising from perspective can be entirely eliminated by the proper interpretation of the picture. Although these errors can exist it should be noted that their presence could not have given rise to the adverse criticism, because this criticism has been based on alleged errors in judging the first horse, whereas these admitted small errors can occur only in connection with the placing of the second and third horses.

WASHINGTON, February 3, 1937.

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STUDIES ON A PORTION OF THE SYSTEM: CaO–Al_2O_3–Fe_2O_3

By Howard F. McMurdie

ABSTRACT

A study has been made of the solidus and liquidus relations in the area CaO–$4CaO.Al_2O_3.Fe_2O_3$–$CaO.Al_2O_3$. Special attention has been given to the study of solid solutions. It was found that $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $CaO.Al_2O_3$ all take into solid solution Fe_2O_3 up to 2.5 percent. The $4CaO.Al_2O_3.Fe_2O_3$ also takes between 3 and 5 percent of the calcium aluminates into solution. In some cases the solid solution relations are such as to shift the conjugation lines away from the joins.

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I. INTRODUCTION

Phase-equilibrium studies[1] on many of the systems involving oxides occurring in significant amounts in portland cement clinker have shown which compounds are formed when mixtures of these oxides are crystallized under equilibrium conditions. Recently several investigators[2] have pointed out the possibility, and outlined the results, of disequilibrium conditions during cooling of the clinker. Others[3] have found by X-ray and optical methods that some of the principal constituents of clinker contain detectable and important amounts of other constituents in solid solutions. Insley found by a quantitative microscopic analysis of commercial clinker that the relative amounts of the compounds actually present often differ widely from the amounts calculated[4] from a chemical analysis.

[1] R. A. Rankin and F. E. Wright, Am. J. Sci. [IV] **39**, 1 (1915); W. C. Hansen, L. T. Brownmiller, and R. H. Bogue, J. Am. Chem. Soc. **50**, 396 (1928).
[2] F. M. Lea and T. W. Parker, Build. Research Tech. Pap. 16 (1935); L. A. Dahl, Rock Products **36** (December 10, 1932).
[3] Herbert Insley, J. Research NBS **17**, 353 (1936) RP917; H. E. Schweite and W. Bussem, Tonind. Ztg. **56**, 801 (1932).
[4] R. H. Bogue, Ind. Eng. Chem. Anal. Ed. **1**, 192 (1929).

Because of these evidences of solid solutions in cement, the National Bureau of Standards has begun a study to determine which solid solutions may occur among the compounds present. In the original paper by Hansen, Brownmiller, and Bogue[5] on the system $CaO-Al_2O_3-Fe_2O_3$, in which discovery of the important compound $4CaO.Al_2O_3.Fe_2O_3$ was announced, it was stated that, in the presence of Fe_2O_3, the indices of refraction of $CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $3CaO.Al_2O_3$ were raised and that further work was necessary to outline the solid solutions involved. The principal purpose of this investigation is to determine the kind and amount of solid miscibility in the area $CaO-4CaO.Al_2O_3.Fe_2O_3-CaO.Al_2O_3$, and, as a first step, that portion of interest in cement technology was reexamined. The relation of the area studied to the ternary system $CaO-Al_2O_3-Fe_2O_3$ is shown in figure 1.

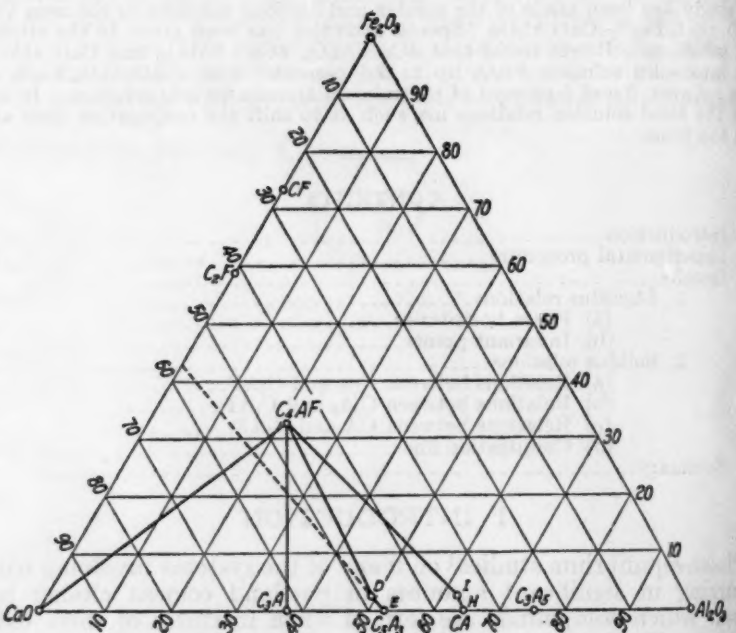

FIGURE 1.—*Relation of the area* $CaO-4CaO.Al_2O_3.Fe_2O_3-CaO.Al_2O_3$ *to the ternary system* $CaO-Fe_2O_3-Al_2O_3$.

The conjugation lines of the area are indicated.

II. EXPERIMENTAL PROCEDURE

The raw materials employed in this study were of reagent quality and consisted of precipitated $CaCO_3$ unusually free from alkalies, alumina with a total maximum impurity of less than 0.01 percent, and ferric oxide containing less than 0.004 percent of ferrous iron. Besides these oxides, some previously prepared $CaO.Al_2O_3$, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$ were used. These compounds were made with similar raw materials and were found to be satisfac-

[5] See footnote 1.

torily pure and homogeneous, by microscopic examination and melting-point determinations.

The compositions for study were carefully proportioned, corrections being made for the ignition losses of the starting materials determined at the time of proportioning. They were ground together dry in a mortar. The mixtures were then heated in an electrically heated furnace to about 1,000° C and then reground. In some cases new mixtures were prepared by mixing together previously prepared batches.

Each resistance furnace used was wound with 80-percent platinum–20-percent rhodium wire on a 1-inch refractory tube, and the temperature controls were of the type described by J. Roberts.[6] The thermocouples were standardized by frequent comparison with a standard thermocouple, which was used only in a furnace with a porcelain tube to prevent possible contamination from the windings.

The liquids with indices higher than 1.74 used to determine the indices of $4CaO.Al_2O_3.Fe_2O_3$ were solutions of sulphur and methylene iodide in phosphorus. These were made as described by C. D. West[7] and were standardized by the minimum deviation method.

For determining primary phase boundaries the quench method was used. Since this method has been discussed in many previous papers,[8] a description is unnecessary here.

Some difficulty was encountered with mixes high in $4CaO.Al_2O_3.Fe_2O_3$ because of crystallization during quenching. It was found that folding the platinum foil so that a point was formed on the bottom gave better results since the quench dropped deeper into the mercury. When quench growths occurred they usually could be distinguished from equilibrium crystals. However, the rapid crystallization of $4CaO.Al_2O_3.Fe_2O_3$ makes it difficult to determine with precision the limits of its primary phase field.

To study the solid solution present, a small amount (about 0.5 g) of the mixture under investigation was heated in a platinum foil envelope to a temperature such that all or at least a large part of the material was liquid. The furnace was then cooled slowly over a period of from 5 to 20 hours to a temperature below the solidus. This method gave nearly complete equilibrium at all times, and crystals in the final products were large enough to be studied and identified by means of the microscope. In some cases glasses of the desired composition were heated for several hours below the solidus to be certain that maximum solution had been obtained. This method produced such small crystals that the number of phases present could be determined but the crystals could not be studied properly.

Insignificant reduction of the ferric oxide was shown in two ways: first, the absence of compounds other than those known to be present in the system $CaO–Al_2O_3–Fe_2O_3$ and, second, similarity in the phase composition of specimens of the same mix heated for long and for short periods at high temperature.

The binary system $CaO–CaO.Al_2O_3$, which forms one side of this area, was worked out by Rankin and Wright.[9] This work was not repeated. The composition and temperature of the eutectic between

[6] J. Optical Soc. Am. **11**, 171 (1925).
[7] Am. Mineral **21**, 245 (1936).
[8] G. W. Morey, J. Wash. Acad. Sci. **13**, 326 (1923); E. S. Shepard, R. A. Rankin, and F. E. Wright, Am. J. Sci. [IV] **28**, 293 (1909).
[9] Am. J. Sci. [IV] **39**, 1 (1915).

CaO and $4CaO.Al_2O_3.Fe_2O_3$ were taken as reported by Hansen, Brownmiller, and Bogue.[10]

In this report, as in others of similar nature, a system of abbreviations is used in referring to the compounds as follows:

$C=CaO$; $F=Fe_2O_3$; $A=Al_2O_3$; thus $C_4AF=4CaO.Al_2O_3.Fe_2O_3$.

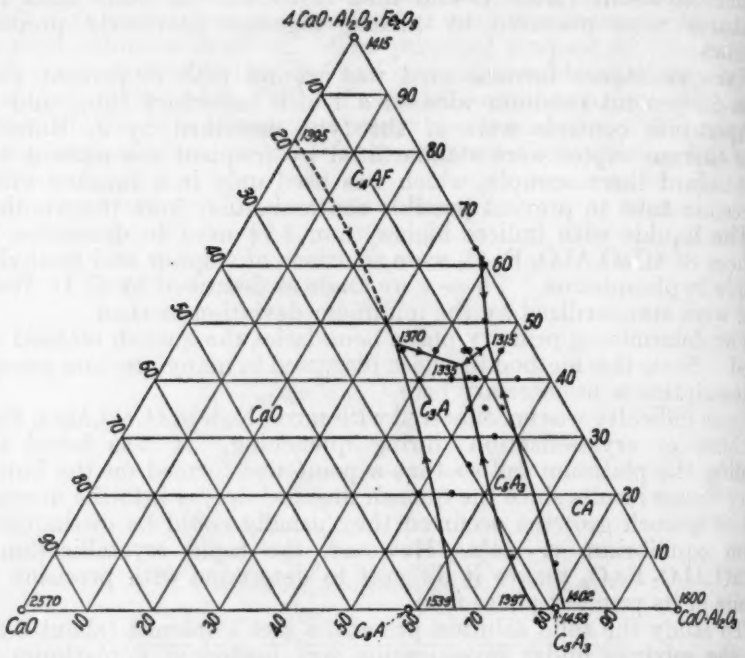

FIGURE 2.—*Liquidus relations in the area* $CaO–4CaO.Al_2O_3.Fe_2O_3–CaO.Al_2O_3$.

III. RESULTS

1. LIQUIDUS RELATIONS

(a) PHASE BOUNDARIES

Figure 2 represents the primary phase fields in the area and the location of the mixes studied. Table 1 gives the composition of the mixes and the results of the quenches. For ready reference to figure 2 the compositions are given in terms of the oxides and of the compounds at the apices of the triangle.

[10] See footnote 1.

TABLE 1.—*Composition and results of quenched mixes*

Mix	Composition						Quenching temperature ±5° C	Phases present
	Fe_2O_3	Al_2O_3	CaO	C_4AF[1]	CA[1]	CaO[1]		
	%	%	%	%	%	%		
1	13.2	40.7	46.1	40	50	10	1,330	Glass+C_3A_3.
							1,320	Glass+C_3A_3+C_4AF.
							1,312	C_3A_3+C_4AF+CA.
2	11.6	42.9	45.5	35	55	10	1,340	Glass+C_3A_3.
							1,325	Glass+C_3A_3+C_4AF.
3	13.2	43.9	42.9	40	55	5	1,335	Glass+CA.
							1,320	Glass+CA+C_4AF.
4	14.8	41.8	43.4	45	50	5	1,340	Glass+CA.
							1,330	Glass+CA+C_4AF.
5	11.5	39.7	48.8	35	50	15	1,345	Glass+C_3A.
							1,340	Glass+C_3A+C_3A_3.
6	8.3	40.7	51.0	25	55	20	1,370	Glass only.
							1,365	Glass+C_3A.
							1,350	Glass+C_3A.
							1,345	Glass +C_3A+C_3A_3.
7	16.5	39.6	43.9	50	45	5	1,340	Glass only.
							1,330	Glass+CA+C_4AF.
8	13.2	37.5	49.3	40	45	15	1,360	Glass+C_3A.
							1,350	Glass+C_3A+C_4AF.
9	14.8	38.6	46.6	45	45	10	1,345	Glass only.
							1,335	Glass+C_4AF.
							1,330	Glass+C_4AF+C_3A_3.
10	14.8	35.4	49.8	45	40	15	1,375	Glass only.
							1,370	Glass+C_4AF.
							1,365	Glass+C_4AF+C_3A.
11	13.2	34.3	52.5	40	40	20	1,390	Glass+C_3A.
							1,375	Glass+C_3A.
							1,365	Glass+C_3A+C_4AF.
12	14.8	32.1	53.1	45	35	20	1,380	Glass+C_3A.
							1,360	Glass+C_3A+C_4AF.
13	6.6	36.5	56.9	20	50	30	1,500	Glass+CaO.
14	6.6	39.7	43.7	20	55	25	1,480	Glass+C_3A.
23	13.1	39.1	47.7	40.0	47.5	12.5	1,340	Glass only.
							1,335	Glass+C_3A_3.
							1,330	Glass+C_3A_3+C_4AF.
24	13.2	39.7	47.1	40.0	48.5	11.5	1,345	Glass only.
							1,340	Glass+C_3A_3.
							1,335	Glass+C_3A_3+C_4AF.
							1,320	Glass+C_3A_3+C_4AF.
							1,310	C_3A_3+C_4AF+CA.
25	14.8	38.2	47.0	45.0	44.5	10.5	1,360	Glass only.
							1,350	Glass+C_4AF.
							1,325	Glass+C_4AF+C_3A_3.
19	3.0	47.0	50.0	9.1	69.6	21.3	1,390	Glass+C_3A_3.
26	2.5	51.0	46.5	7.6	76.4	16.0	1,423	Glass only.
							1,408	Glass+CA.
44	20.7	37.2	42.1	63.0	37.0	------	1,355	Glass+C_4AF.
							1,350	Glass+C_4AF+CA.
45	17.7	38.4	41.9	60	40.0	------	1,355	Glass+CA.
							1,350	Glass+CA+C_4AF.
29	10.0	42.8	47.2	30	56.5	13.5	1,350	Glass only.
							1,340	Glass+C_3A_3.
							1,330	Glass+C_3A_3+C_4AF.
59	11.5	41.2	47.3	35	52.5	12.5	1,340	Glass+C_3A_3.

[1] Composition is given in terms of C_4AF, CA, and CaO to permit ready identification of the points in figure 2.

As compared with the original report [11] on this system, the present investigation shifts the boundaries between the field of C_4AF and the fields of C_3A, C_5A_3, and CA much farther toward the C_4AF apex. For instance, in the present work the invariant point for C_4AF, C_3A, C_5A_3 and liquid is placed at CaO 38, Al_2O_3 48, and Fe_2O_3 14 percent, whereas in the original paper it is located at CaO 47, Al_2O_3 43, and Fe_2O_3 10 percent. F. M. Lea [12] also reports quenches which confirm in general the location of the boundaries as shown in figure 2.

Since solid solutions occur in this area, not all crystallization paths are straight lines from the starting point to the boundary curves. During cooling the solid phase in equilibrium with the liquid is not of constant composition; therefore, the course of liquid composition must deviate from a straight line so that it will at all times lie on the line determined by the point of origin and the composition of the solid phase in equilibrium with it.

(b) INVARIANT POINTS

Three ternary invariant points were determined in the course of the work. Their composition and temperatures are given in table 2.

TABLE 2.—*Ternary invariant points*

Liquid and vapor in equilibrium with—	Composition						Temperature (±5° C)
	Fe_2O_3	Al_2O_3	CaO	C_4AF	CA	CaO	
	%	%	%	%	%	%	°C
CaO–C_4AF–C_3A	15	32	53	46	34	20	1,370
C_4AF–C_3A–C_5A_3 [1]	14	38	48	42	46	12	1,333
C_4AF–C_5A_3–CA [1]	15	40	45	46	48	6	1,315

[1] Eutectic.

2. SOLIDUS RELATIONS

Table 3 gives the composition and the results of slow crystallization of samples used to study the solid solutions. In the discussion of these results the terms "join" and "conjugation line" are used. A join is the straight line drawn between two compounds, and it may be of no more significance. A conjugation line is the line which separates areas in which the final phases resulting from equilibrium crystallization are different. As a general rule, conjugation lines are identical with possible joins, but in parts of this system it is found that they are not, as will be discussed later.

[11] W. C. Hansen, L. T. Brownmiller, and R. H. Bogue, J. Am. Chem. Soc. **50**, 396 (1928).
[12] F. M. Lea. Private communication (November 20, 1936).

TABLE 3.—*Final products of slow crystallization.*

Mix	Composition (by weight)						Phases present (*ss*=solid solution)
	Fe_2O_3	Al_2O_3	CaO	C_4AF	CA	CaO	
	%	%	%	%	%	%	
16	2.5	47.5	50.0	7.6	71.0	21.4	C_3A_3 (*ss*)+C_3A (*ss*).
17	2.5	49.5	48.0	7.6	74.2	18.2	C_3A_3 (*ss*)+CA (*ss*).
18	2.5	48.5	49.0	7.6	72.6	19.8	C_3A_3 (*ss*) only (index 1.620±0.002).
19	3.0	47.0	50.0	9.1	69.6	21.3	C_3A_3 (*ss*)+C_3A (*ss*)+C_4AF (*ss*).
20	2.5	43.7	53.8	7.6	65.2	27.2	C_3A_3 (*ss*)+C_3A (*ss*)+trace C_4AF.
21	3.0	34.0	63.0	9.1	49.6	41.3	C_3A (*ss*)+CaO+C_4AF.
22	2.8	53.2	44.0	8.5	79.5	12.0	C_3A_3 (*ss*)+CA (*ss*)+trace of C_4AF.
24	13.2	39.7	47.1	[1] 40.0	------	------	C_3A_3 (*ss*)+C_4AF (*ss*)+CA (*ss*).
26	2.5	51.0	46.5	7.6	76.4	16.0	C_3A_3 (*ss*)+CA (*ss*).
27	2.6	49.7	47.7	[1] 8.0	------	------	C_3A_3 (*ss*)+CA (*ss*)+trace of C_4AF.
28	3.3	49.1	47.6	10.0	------	------	C_3A_3 (*ss*)+CA (*ss*)+C_4AF.
29	10.0	42.8	47.2	[1] 30.0	------	------	C_3A_3 (*ss*)+CA (*ss*)+C_4AF.
30	31.3	22.6	46.1	[1] 95.0	------	------	C_4AF (*ss*).
33	1.6	50.7	47.7	[2] 5.0	------	------	C_3A (*ss*) (index 1.72±0.002).
34	2.5	36.5	61.0	[2] 7.5	------	------	C_3A (*ss*)+C_4AF.
37	30.9	22.9	46.2	[1] 94.0	------	------	C_4AF (*ss*)+small amount of C_3A_3.
38	31.6	21.7	46.7	[2] 96.0	------	------	C_4AF (*ss*)+trace of C_3A.
40	1.8	43.6	54.6	5.6	65.7	28.7	C_3A_3 (*ss*)+C_3A (*ss*).
41	1.5	35.9	62.6	4.6	54.2	41.2	C_3A (*ss*)+CaO.
42	29.7	25.4	44.9	90.0	10.0	------	C_4AF (*ss*)+CA.
46	31.3	23.2	45.5	95.0	5.0	------	C_4AF (*ss*) only.
47	30.4	24.3	45.3	92.5	7.5	------	C_4AF (*ss*)+small amount of CA.
48	1.6	62.5	35.9	5.0	95.0	------	CA (*ss*)+C_3A_3.
49	3.3	60.2	36.5	10.0	90.0	------	CA (*ss*)+C_3A_3+C_4AF.
50	2.5	61.3	36.2	7.5	92.5	------	CA (*ss*)+C_3A_3.
51	2.5	63.0	34.5	------	[3] 97.5	------	CA (*ss*) only.
52	5.0	61.3	33.7	------	[3] 95.0	------	CA (*ss*)+C_3A_3+C_4AF.
53	3.75	62.15	34.1	------	[3] 96.25	------	CA (*ss*)+C_3A_3+C_4AF.
54	3.0	56.7	40.3	9.1	85.7	5.2	CA (*ss*)+C_3A_3 (*ss*)+small amount of C_4AF.
55	3.3	54.6	42.1	10.0	81.3	8.7	CA (*ss*)+C_3A_3 (*ss*)+small amount of C_4AF.
56	4.1	60.8	35.1	------	[4] 95.9	------	CA (*ss*)+C_4AF.
57	2.1	62.7	35.2	------	[4] 97.9	------	CA (*ss*) only.
58	3.1	61.7	35.2	------	[4] 96.9	------	CA (*ss*)+C_4AF.

[1] On join $C_4AF–C_3A_3$.
[2] On join $C_4AF–C_3A$.
[3] On join $CA–Fe_2O_3$.
[4] On join CA–CF.

Figure 3 indicates the joins, conjugation lines, and limits of solid solution. Figure 1 shows the conjugation lines of the area on a diagram of the full ternary system $CaO–Al_2O_3–Fe_2O_3$. It is seen that there is solid solution of Fe_2O_3 in each of the three calcium aluminates. The ratio in which the various compounds take up Fe_2O_3 and lime varies and the relations between each compound and C_4AF are discussed separately.

(a) RELATIONS BETWEEN C_3A AND C_4AF

On the join $C_3A–C_4AF$ the solid solution is of a simple nature. C_3A takes up to 5 percent of C_4AF in solution; thus a mix of composition *A* (fig. 3) crystallizes to a single phase of its own composition. The index of refraction of C_3A, when pure, is 1.71, that of the composition *A* is 1.720+0.002.

C_4AF takes up between 2.5 and 5 percent of C_3A. This appears to lower the indices of C_4AF very little. Any composition on the join from *L* to *A* will crystallize to these two solid solutions. This join is not a binary system since C_3A melts to CaO and liquid, and CaO is the primary phase over a large part of the join.

(b) RELATIONS BETWEEN C_5A_3 AND C_4AF

Mixes on the join C_5A_3–C_4AF do not give these two compounds alone on crystallization. In such mixes C_5A_3 takes Fe_2O_3 and CaO into solid solution, the CaO and Fe_2O_3 being in the ratio indicated by the intersection of the line *ED* (fig. 1) extended, with the CaO–Fe_2O_3 side, leaving a liquid deficient in lime to form only C_4AF and C_5A_3 and from which (fig. 3) some CA crystallizes at equilibrium. Any mix between *E* and *D* (fig. 2) will give a single phase. The index of refraction of pure C_5A_3 is 1.608, that of the composition *D* is 1.620 $\pm$0.002. Any mix on the join between *F* and *E* will crystallize to

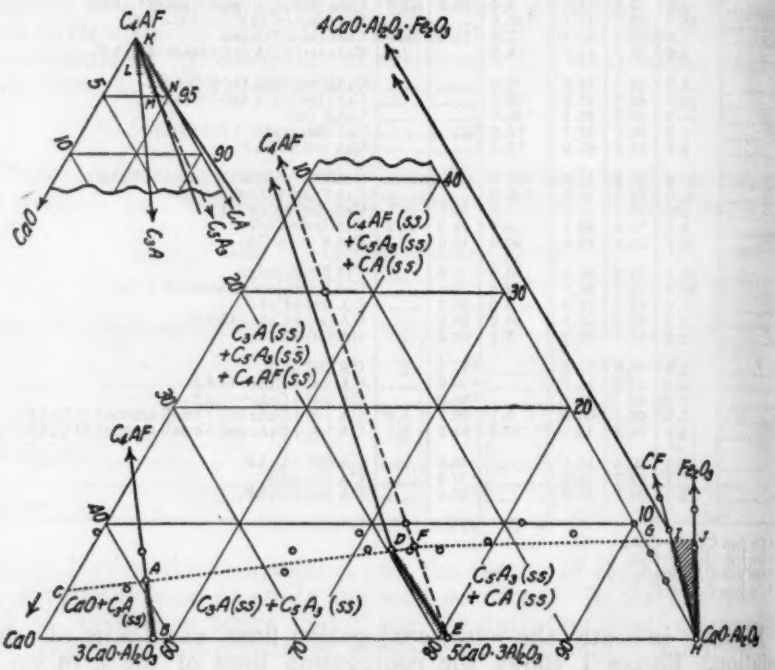

FIGURE 3.—*Solidus relations in the area* CaO–4CaO.Al_2O_3.Fe_2O_3–CaO.Al_2O_3, *showing the lines and areas of solid solution and the joins and conjugation lines.*

two phases, a solid solution of C_5A_3 of a composition between *D* and *E* and a solid solution of CA.

C_4AF may take up about 5 percent of C_5A_3 into solid solution, thus lowering the indices of refraction (N_D) of C_4AF to α 1.94$\pm$0.01, γ 1.99$\pm$0.01. The pure material has the indices α 1.98$\pm$0.01 and γ 2.07$\pm$0.01. Any composition on this join between *M* and *F* will give, on complete crystallization, C_5A_3 (*ss*)[13] of composition *D*, C_4AF (*ss*) of composition *M*, and CA (*ss*) of composition *I*.

(c) RELATIONS BETWEEN CA AND C_4AF

Mixes on the join CA and C_4AF do not give these two compounds alone on complete crystallization, but have a relation similar to that between C_5A_3 and C_4AF. In this case, CA takes Fe_2O_3 and CaO into

[13] Solid solution, abbreviated *ss*.

solid solution, seemingly in the ratio of CaO. Fe_2O_3, as indicated by the line *HI*. This results in a liquid deficient in Al_2O_3 to form only C_4AF and CA, therefore C_5A_3 is formed from mixes on this join. Any mix between *H* and *I* will crystallize to a single phase. Pure CA had indices of $\alpha=1.643$, $\gamma=1.663$. The CA (*ss*) of composition *I* has indices of $\alpha\,1.650\pm0.002$, $\gamma\,1.667\pm0.002$. Mixes on the join CA–Fe_2O_3 (the line *HJ*) with less than 2.5 percent of Fe_2O_3 also crystallize to a single phase and, therefore, any composition in the triangle *IHJ* on crystallization forms a single homogeneous phase consisting of solid solutions of CF and Fe_2O_3 in CA. Any mix on the join CA–C_4AF between *H* and *G* will crystallize to two phases, a solid solution of a composition between *H* and *I* and a solid solution of a composition between *E* and *D*.

C_4AF takes about 5 percent of CA into solid solution. This lowers the indices of refraction about the same as does the solid solution of 5 percent of C_5A_3.

(d) CONJUGATION LINES

Since two [14] of the equilibrium crystalline products produced in this system are not pure compounds or of compositions lying on joins of the system, it is necessary to draw the conjugation lines in positions different than the joins. Thus the line dividing the area in which the final products are C_4AF (*ss*), C_3A (*ss*) and C_5A_3 (*ss*) from that in which they are C_4AF (*ss*), C_5A_3 (*ss*) and CA (*ss*) will pass through the point *D* rather than along the join $C_4AF-C_5A_3$. Similarly, the line dividing the area in which the final products are C_4AF (*ss*), C_5A_3 (*ss*) and CA (*ss*) from that in which they are C_4AF (*ss*), CA (*ss*), and C_3A_5 (*ss*) must pass through the point *I* rather than along the join C_4AF-CA.

Because of the small range of composition within the solid solution area near the C_4AF apex the compositions between the conjugation lines were not studied. It is reasonable to assume that the area *KNML* (fig. 3) is one in which one phase only results from crystallization.

The line *CADG* across figure 3 indicates the limit of compositions which form only two phases on complete crystallization. All mixes containing a greater amount of ferric oxide produce three phases, one of which is C_4AF (*ss*).

The join $CA-C_4AF$ is neither a conjugation line nor a binary system, therefore the point where the boundary between the primary phases of CA and C_4AF (fig. 2) crosses the join is of no significance. Also, since the area $CaO-C_4AF-CA$ is not bounded by three binary systems, this area is not a true ternary system.

X-ray diffraction patterns have been made of the solid solutions of C_3A, C_5A_3, and CA and all showed slight but distinct shifts in the crystal lattice.

[14] The solid solution of the aluminates in C_4AF is assumed to be such that the composition of the resulting C_4AF(*ss*) lies on a join.

IV. SUMMARY

The solidus and liquidus relations in the area $CaO-4CaO.Al_2O_3.Fe_2O_3-CaO.Al_2O_3$ have been determined. Limited solid solutions between the iron compound and the three calcium aluminates were encountered. The solution was in some cases of a type that shifted the conjugation lines away from the joins. $4CaO.Al_2O_3.Fe_2O_3$ takes between 3 and 5 percent of the calcium aluminates in solid solution.

The author wishes to express his thanks to Dr. Herbert Insley for help and advice during the work and to R. H. Ewell, who prepared some of the mixes used.

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EFFECT OF THE DEPTH OF DRILLED PORTS ON THE LIMITS OF OPERATION OF DOMESTIC GAS BURNERS

By John H. Eiseman and Francis A. Smith

ABSTRACT

This paper describes the effect of variations in the depth of the metal through which the ports are drilled on the limits of operation of domestic gas burners. Quantitative data are presented showing the effect of varying the depth of port from 1½ in. to 1/32 in. on the limits of flash back, blowing, and yellow tips, as well as on the proportion of primary air injected. These data were obtained with two gases of different composition and with four different port sizes. The effect of turbulence on the position of the burner limits is also discussed. The results obtained indicate that a compromise between all the factors involved might result in the selection of a port ¼ in. in depth as the most practicable.

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I. INTRODUCTION

For a number of years the Gas Chemistry Section of the National Bureau of Standards has been engaged in a study of the performance of domestic gas-burning appliances.

Nearly all gas burners employed in domestic appliances are so designed that a portion of the air necessary for complete combustion mixes with the gas before it reaches the burner ports. This is called "primary" air. The additional air required is secured from the atmosphere surrounding the flames and is termed "secondary" air. As the amount of primary air which mixes with a given amount of gas is increased, a limit is reached above which the flames either blow away from the ports or flash back into the burner, depending on the

gas rate used. Similarly, if the proportion of primary air is decreased, a limit is reached below which the color of the tip of the inner cone of the flame becomes yellow. It is obvious that unsatisfactory burner operation will result if any one of these three limits is exceeded. A more complete discussion of these limits and their determination is given in two previous papers.[1] [2]

It is apparent that it is desirable to design a burner so that the satisfactory working range between these limits of operation is as great as possible. Some of the factors which affect the position of these limits, and which must be considered because of their consequent effect upon the safe working range, are as follows: (*a*) the composition of the gas (with natural gas the flames are more likely to blow off the ports than to flash back through them, while with manufactured gas the reverse is true); (*b*) the size of the port (increasing the port size decreases the trouble from the blowing of the flames, while decreasing the port size tends to prevent their flashing back); (*c*) the altitude (appreciable decreases in barometric pressure) at which the burner is used; (*d*) the burner temperature; and (*e*) the smoothness and direction of the channels within the burner casting. A discussion of the effects of some of these factors has also appeared in previous papers.[3]

That a deep port tends to prevent the flames from flashing back has long been known, but no definite information has been available regarding the extent of this action, or regarding other effects, either beneficial or adverse, which might result from the use of deep ports, on the other limits of burner operation.

This paper presents the quantitative relationships which have been found to exist between the depth of drilled ports and the positions of the several limits of operation of a domestic gas burner.

II. EQUIPMENT AND METHOD OF TEST

The gas for the majority of these tests was the mixed natural and manufactured supply now being distributed in Washington, D. C., a gas of 600 Btu and 0.67 specific gravity (referred to air).[4] This heating value is maintained by the local gas company by means of a calorimetric proportioning machine. This machine automatically varies the proportions of the natural and manufactured gases as their heating values fluctuate, so that the resulting mixture always has a heating value of 600 Btu per cubic foot. This method insures a constant heating value, but the composition remains variable. Since small variations in the properties of the gas, which would be unimportant from the standpoint of service, might tend to mask the effect of changing from one depth of port to another, it was necessary to use a gas which was as nearly as possible of constant composition as well as of constant heating value. The variation in composition which is the most likely to affect the position of the limits of burner operation is a change in the proportion of hydrogen in the mixture.

[1] *Method of testing gas appliances to determine their safety from producing carbon monoxide.* BS Tech. Pap. **20**, 125 (1925) T304.

[2] *A method for determining the most favorable design of gas burners.* BS J. Research **8**, 669–709 (1932) RP446.

[3] *The effect of altitude on the limits of safe operation of gas appliances.* BS J. Research **10**, 619–637 (1933) RP553, and also papers cited in footnotes 1 and 2.

[4] The following is a representative analysis of the Washington, D. C., mixed gas for the period covered by these tests: CO_2, 4.1%; "Illuminants", 2.4%; O_2, 0.2%; CO, 14.2%; H_2, 19.6%; CH_4, 43.8%; N_2, 15.7%. The proportion of natural gas in the mixture averaged a little over 27.5%.

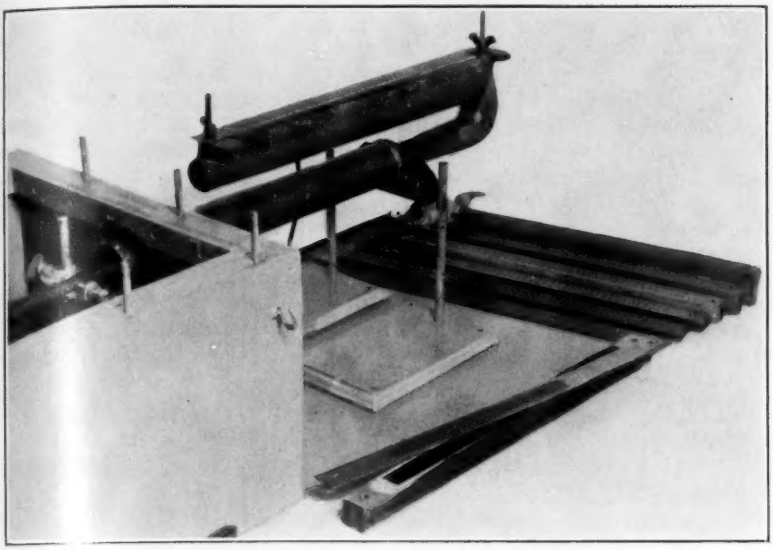

FIGURE 1.—*Burner with 1/32-in. plate attached.*

To the right of the burner are the other plates of the set and in front, with a plate on top of it, is a spacer to increase the volume of the burner head.

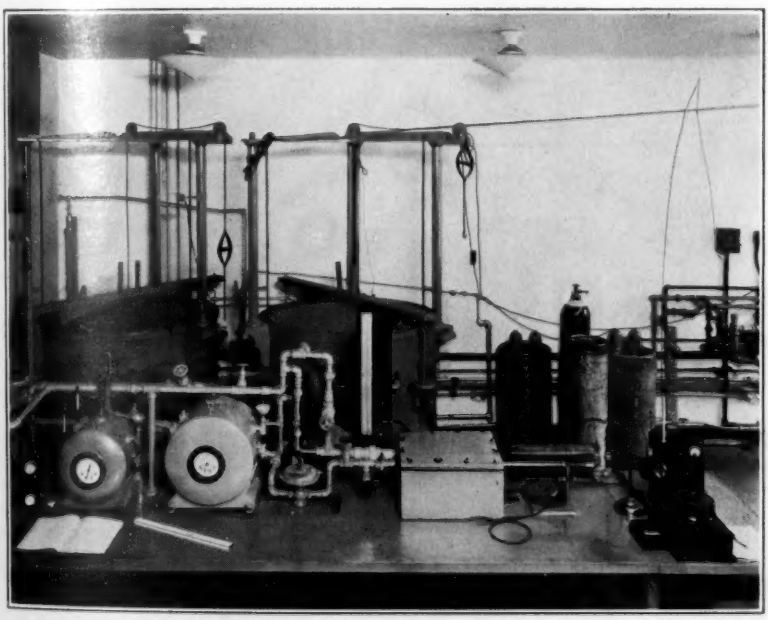

FIGURE 2.—*Equipment used to test gas burners.*

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Since the thermal conductivity of hydrogen is about six times that of most of the other constituents of the gas, a preliminary survey of the extent of this variation was made by following the changes in the thermal conductivity over a period of several weeks. From these results a value was selected which recurred the most frequently. By storing the gas supply in two gas holders of 300 and 500 ft^3 capacity, and following the thermal conductivity of the gas in the city main, it was always possible to replenish the supply with gas having approximately this same thermal conductivity and consequently the same composition. The gas for the tests was always taken from the larger of these two holders while the gas to replenish the supply was added to the smaller from the city main. At the end of each day the larger holder was refilled from the smaller.

A few tests were also made with a natural gas having a heating value of 1,170 Btu per cubic foot to determine whether a gas of radically different composition would alter the relative effect of changes in port depth.

In order to determine the effect of changing the depth of the port without at the same time changing any of the other parts of the burner, the following procedure was adopted. A radiant heater burner of the so-called "saxophone" type was selected and the top carefully milled off. Steel plates of the same size as the original burner top, but of various thicknesses (1/32, 1/16, 1/8, 1/4, 1/2, 3/4, 1, and 1 1/2 in., respectively), were then made and each drilled with 62 ports. By means of a bolt at each end of the burner, and a thin film of metal cement, it was possible to attach any of the plates to the burner casting.

Figure 1 shows the burner with the 1/32-in. plate attached. To the right of the burner are the other plates of the set and in front, with a plate on top of it, is the spacer which will be discussed later in the paper.

Four complete sets of these plates were made, each set having the same number of ports but differing in their size, so that any variations introduced (by the changes in port size) into the effect of the depth of the port on the positions of the limits could also be determined. The four drill sizes used were nos. 40, 36, 32, and 28 (drill manufacturers' standard, having diameters of 0.0980, 0.1065, 0.1160, and 0.1405 in., respectively).

The orifice used was selected to give the normal rate of gas flow for this size and style of burner (226 Btu per hour per port) at the "test pressure" for manufactured gas adopted by the American Gas Association, 3.5 in. of water. The same orifice was used for all tests, except those on natural gas,[5] so that any variation in the position of the normal air injection curve for any one gas is the result of differences in the port only. Figure 2 shows the apparatus used for these tests.[6] Having the burner installed as shown and burning gas at a constant rate, the primary air was increased until the flames either lifted from the ports or flashed back into the burner. When this condition was reached, the relative proportion of air and gas was determined. The

[5] For the tests using natural gas, an orifice was used that delivered the normal rate of 226 Btu per hour per port at a pressure of 7.0 in. of water.

[6] A detailed description of this apparatus is given in the Bureau of Standards Research Paper 446 (BS J. Research 8, 669–700, 1932).

primary air was next decreased until yellow appeared in the flame, and the ratio of air to gas again determined. The gas rate was then changed and the same procedure repeated until a series of tests had been made which covered a range of gas rates from one and one-half times that normally used down to the lowest possible "turn-down." A determination of the normal air injection was then made over the same range of gas rates. The results obtained were plotted, using as coordinates "Gas rate—Btu per hour per port" and "Primary air—percent of total air required."

In figure 3, the curves indicate the position of the boundaries of the regions in which flash back, blowing, and yellow tips occur with the mixed gas described above when using the ¼-in. plate of the set having no. 36 ports. Figure 3 also shows the shape and position of the curve

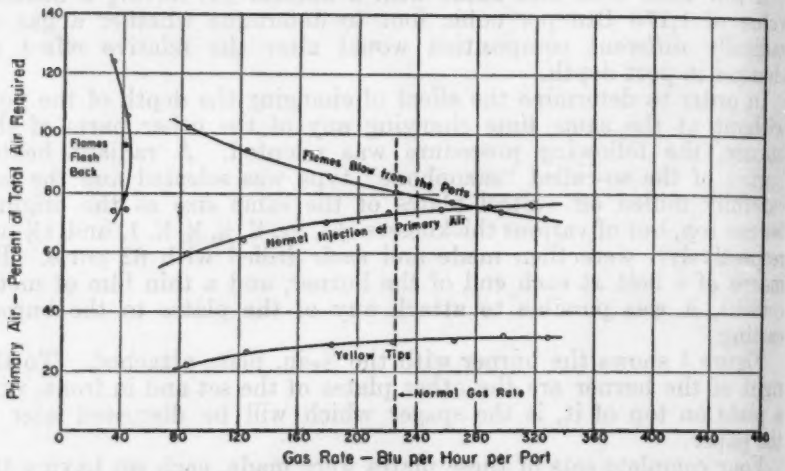

FIGURE 3.—*Limits of satisfactory operation of the ¼ in. depth of port (no. 36 drill size) with Washington, D. C., mixed gas.*

indicating the normal injection of primary air obtained with this plate. Curves similar to those of figure 3 were obtained for each of the other plates of this set.

A set of curves summarizing the results obtained from the eight plates of this set is shown in figure 4. In this figure the depth of the port, in inches, is plotted as abscissa. The ordinate is "Primary air—percent of total air required." The primary air at the normal gas rate [7] (226 Btu per hour per port) was taken from the blowing curve, the normal injection curve, and the yellow-tips curve of figure 3, and the three points were plotted in figure 4 on the vertical coordinate line corresponding to the ¼-in. depth of port. From curves similar to those of figure 3, obtained with the seven other plates of the set, similar points were plotted in positions corresponding to the depths of the respective ports. Smooth curves were then drawn through the points, representing, for each of the three limits mentioned, the primary air (at the normal gas rate) at which the respective limits were encountered with the various depths of port.

[7] Since the curves like those shown in figure 3 for the various depths of port all parallel one another closely, a summary curve derived by selecting the primary air at any other gas rate than the normal would be entirely similar in shape and slope but displaced slightly in its vertical position.

In the case of the flash-back limit the maximum gas rate, in figure 3, at which flash back occurred (47 Btu per hour per port) is plotted in figure 4 at 47 on the ordinate for the ¼-in. depth. The same numerical scale serves for maximum gas rate in the case of flash back and for primary air in the case of the other three limits. The maximum gas rates at which flash back occurred with the other depths of port were taken from the curves similar to those of figure 3 and plotted in figure 4 in the manner just described. A smooth curve was then drawn through the points as before.

These curves indicate the manner in which these various limits shift as the depth of the port is varied, all other conditions remaining constant.

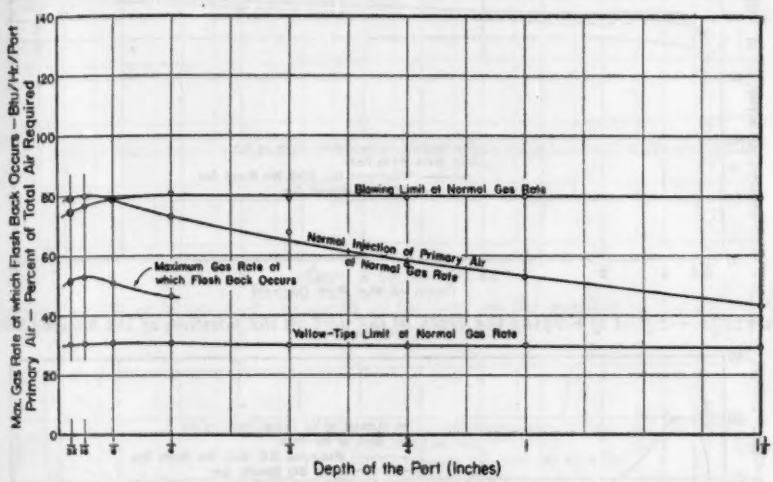
Max. Gas Rate at which Flash Back Occurs – Btu/Hr./Port
Primary Air – Percent of Total Air Required
140
120
100
80
60
40
20
0
Blowing Limit at Normal Gas Rate
Normal Injection of Primary Air at Normal Gas Rate
Maximum Gas Rate at which Flash Back Occurs
Yellow-Tips Limit at Normal Gas Rate
Depth of the Port (Inches)

FIGURE 4.—*Summary of the results from curves similar to those of figure 3, showing the effect of varying the depth of the port on the positions of the several limits.*

Normal gas rate of 226 Btu per hour per port. Drill size, no. 36.

III. DISCUSSION OF THE RESULTS

In order to avoid the possibility of drawing false conclusions and to insure the applicability of the conclusions drawn over a range of port sizes and fuel supplies, an attempt has been made to eliminate from consideration any variations which might result from unknown or uncontrolled variables. For this purpose the curves similar to those of figure 4 for each of the limits studied have been separated from those of the other limits and plotted together in figures 5 to 8. In this way peculiarities and variations common to all, or most, of the curves of a set become evident, and these alone may reasonably be considered as resulting from variations in the depth of the port.

A number of other interesting facts and relationships may be deduced from a study of the curves presented in this paper. For example, the effect (on the limits) of varying the size of the port, which was treated in Research Paper RP446 referred to above, is evident from the relative positions of the curves, but relationships which are not pertinent to the effects of the depth of the port will not be discussed here.

1. EFFECT OF PORT DEPTH ON THE BLOWING LIMIT

An inspection of figure 5 at once discloses that the effect of changing the depth of the port from 1½ in. to ¼ in. is small and constant—all the curves are nearly horizontal straight lines. In the case of the two larger ports (nos. 28 and 32) the flames are blown from the ports a

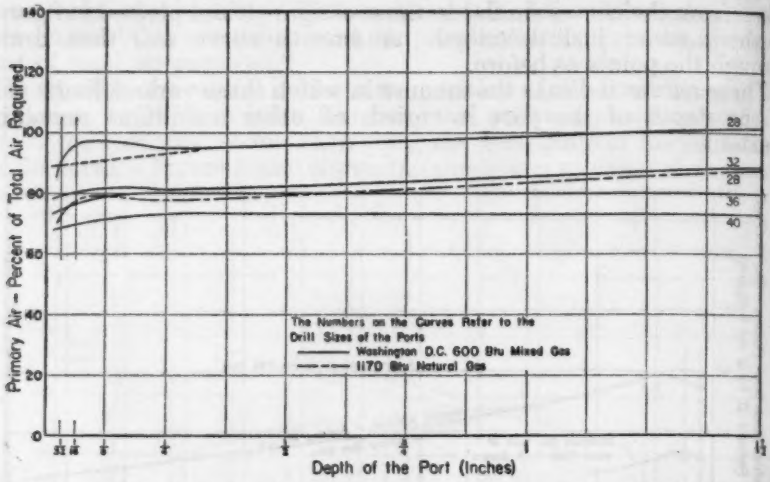

FIGURE 5.—*Effect of varying the depth of the port on the position of the blowing limit.*

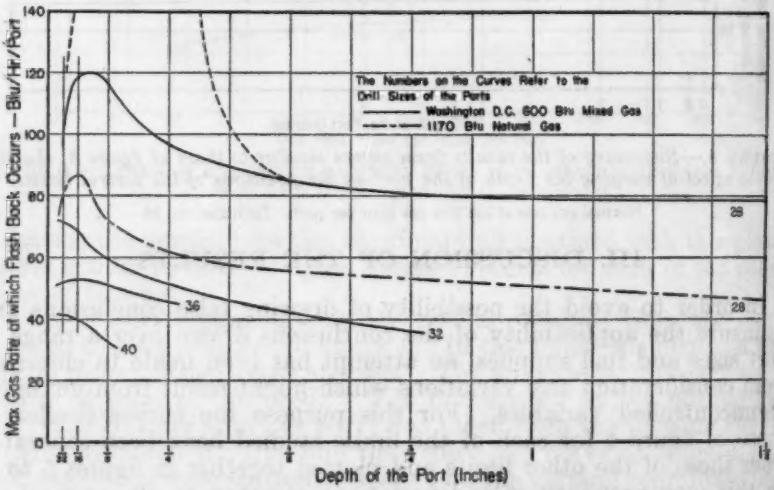

FIGURE 6.—*Effect of varying the depth of the port on the position of the flash-back limit.*

little more readily (the primary air which may be introduced into the mixture is a little less) as the depth of the port decreases.

A slight rise, most marked with the no. 28 port and on both gases, occurs from a depth of ¼ to ⅛ in. All the curves have a distinct downward curvature (i. e., blowing occurs more readily) as the depth approaches 1/32 in. A possible explanation for this downward curvature will be considered after the effects on the other limits have been discussed.

2. EFFECT OF PORT DEPTH ON THE FLASH-BACK LIMIT

It is evident from figure 6 that the effect on the position of the flash-back limit is very slight with ports deeper than ¾ in. and that the effect begins to be considerable only with ports less than ¾ in. deep,

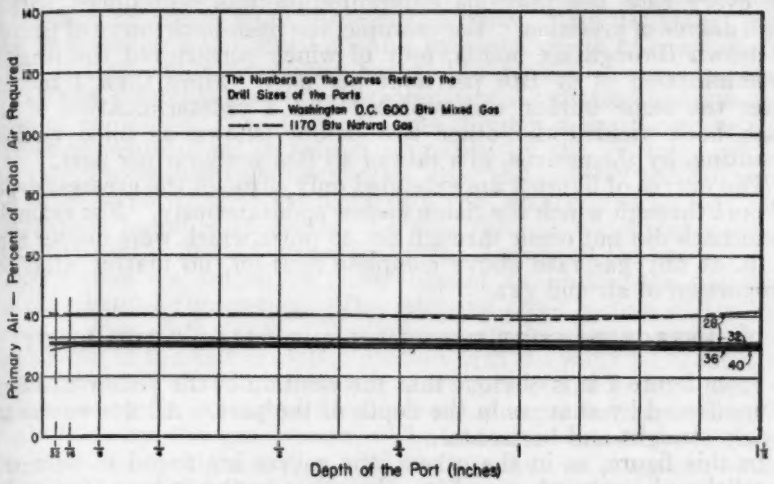
The Numbers on the Curves Refer to the Drill Sizes of the Ports
Washington D.C. 600 Btu Mixed Gas
1170 Btu Natural Gas
Primary Air — Percent of Total Air Required
Depth of the Port (Inches)
28
32
36
40

FIGURE 7.—*Effect of varying the depth of the port on the position of the yellow-tips limit.*

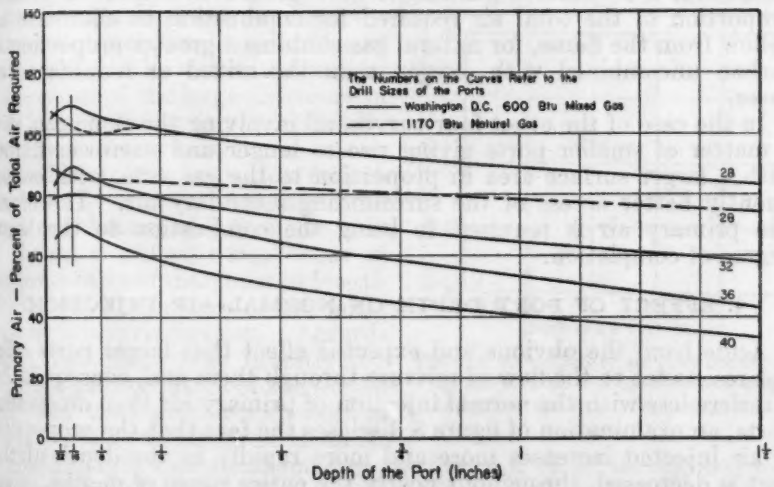
The Numbers on the Curves Refer to the Drill Sizes of the Ports
Washington D.C. 600 Btu Mixed Gas
1170 Btu Natural Gas
Primary Air — Percent of Total Air Required
Depth of the Port (Inches)
28
28
32
36
40

FIGURE 8.—*Effect of varying the depth of the port on the normal injection of primary air.*

when it increases more and more rapidly—the flames flashing back through the ports spontaneously at higher and higher gas rates as the depth is decreased. In the case of three of the curves a downward bend is again noted at the 1/16 in. depth, which is more susceptible to flash back than either the ⅛ or 1/32 in. depths.

Improbable as it seemed when first observed, the effect is a definite one, exhibited by three of the five curves, with a tendency indicated in the case of the other two. These reversals were verified both by immediate repetition and by checks after intervals of several weeks when the gas used had been replaced repeatedly by a fresh supply. In every case the previous determination was reproduced with a high degree of precision. For example, the flash-back curve of figure 3 is drawn through six points, four of which constituted the original determination of 47 Btu per hour per port. More than 4 months later the same burner was replaced and a redetermination of the flash back yielded the other two points (shown as filled circles), resulting, by themselves, in a rate of 45 Btu per hour per port.

The curves of figure 6 are extended only through the greatest depth of port through which the flame flashes spontaneously. For example, flash back did not occur through no. 36 ports which were deeper than ¼ in. at any gas rate above complete shut-off, no matter what the proportion of air and gas.

3. EFFECT OF PORT DEPTH ON THE YELLOW-TIPS LIMIT

From figure 7 it is obvious that the position of the yellow-tips limit is unaffected by changes in the depth of the port. All five curves are nearly straight and horizontal.

In this figure, as in the others, the curves are found to be nearly parallel and arranged one above the other in the order of increasing port size. The reason for this is more or less obvious in the other cases, and here natural gas might be expected to require a greater proportion of the total air required for combustion to eliminate all yellow from the flame, for natural gas contains a greater proportion of carbon uncombined with oxygen than the mixed or manufactured gases.

In the case of the other four curves, all involving the same gas, it is a matter of smaller ports giving rise to longer and narrower flames with a larger surface area in proportion to the gas rate, with consequently better access of the surrounding secondary air. Therefore, less primary air is required to bring the combustion to the same degree of completion.

4. EFFECT OF PORT DEPTH ON NORMAL AIR INJECTION

Aside from the obvious and expected effect that larger ports offer less resistance to the flow of mixture through them and, consequently, interfere less with the normal injection of primary air than do smaller ports, an examination of figure 8 discloses the fact that the proportion of air injected increases more and more rapidly as the depth of the port is decreased, throughout nearly the entire range of depths.

It is again noted that a reversal begins at a depth of 1/16 in., the 1/32 in. depth permitting the injection of less primary air, at the normal gas rate, than the 1/16 in. depth, which appears to permit the maximum injection with the particular set of conditions under which these tests were made. This reversal, however, seems to be absent in the case of the natural gas.

IV. PECULIARITIES OF THE CURVES OF FIGURES 5, 6, AND 8

In searching for an explanation for the reversals of curvature exhibited by many of the curves of figures 5, 6, and 8, with maxima at or near the 1/16 in. depth, it was instructive to consider the mechanism of the flow of the mixture through the ports. The individual port may be considered as a small channel in which length of channel and depth of port are synonymous terms. As such a channel becomes shorter and shorter it loses the characteristics of a channel and assumes those of an orifice. The flow of a gas through a small channel (at a given pressure drop) is limited primarily by the viscosity of the gas. As the channel becomes shorter, the "end effects" become more and more important. Eventually the end effects predominate and the channel becomes an orifice, the flow through which (at a given pressure drop) is limited primarily by the density of the gas.

Just before the transition from channel to orifice, the gas flow fills the channel completely. The effective cross section of the gas stream is that of the port. The velocity in the stream varies from a maximum in the axis to zero in contact with the walls. On shortening the channel, that is, decreasing the depth of the port, a ratio of depth to diameter is reached at which the channel no longer is completely filled by the gas stream. The entrance end of the channel acts like a sharp-edged orifice, and the effective cross section of the stream is that of the vena contracta. The stream of gas is no longer in contact with the walls of the channel and the velocity at the surface of the stream is only slightly less than the average for the whole.

Such a situation was reported for the case of a channel-type orifice of no. 2 drill size in a previous paper.[8] On account of the large difference in size, length of channel, and pressure drop in the two cases, it was uncertain whether the transition (which occurred at a ratio of diameter to length of channel of 2.21 in the case of the no. 2 orifice) would occur at the same ratio of diameter to length of channel in the case of the ports used in this investigation. Accordingly, the effect was investigated with the burner plates of the no. 36 drill size used as multiple orifices having different lengths of channel.

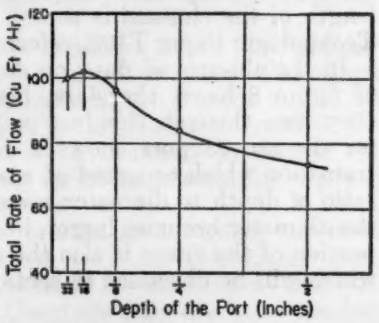

FIGURE 9.—*Effect of varying the depth of the port on the total flow through the ports under a constant pressure drop.*

The gas rate was maintained at the "normal rate" throughout the entire series of tests. The air was adjusted to an average "good adjustment" with the burner of 1/32 in. port depth in place. The drop in pressure through the ports was then determined by means of a sloping manometer, and the sum of the rates of flow of gas and air was determined by metering both.

For subsequent burners of different depth of port the air was set to give the same pressure drop through the ports, and then the total flow through the ports was determined. The total rate of flow is plotted against the depth of the port in figure 9. It is clear that the

[8] BS Tech. Pap. 193 (1921).

flow increases as the depth of the port (i. e., the length of the channel) decreases from ports ½ in. to 1/16 in. in depth. The rate of flow is distinctly less, however, in the case of the port 1/32 in. deep, which indicates not only that the behavior of the curves of figures 5, 6, and 8 can be explained on the basis of a sudden decrease in the flow of mixture through the port 1/32 in. deep as compared with the port 1/16 in. deep, but that the change takes place at approximately the same ratio of diameter to length of channel as in the case of the orifices previously studied.

1. NORMAL INJECTION

In the case of the normal injection of primary air, the reversals in the curves of figure 8 may be accounted for quite readily on the basis of the considerations just outlined.

When the depth of the port was changed from 1/16 in. to 1/32 in., if the transition from capillary flow to orifice flow also took place, a decrease in the effective cross section of the stream of mixture would also take place. Such a decrease in the cross section of the stream issuing from the port must result in a decrease in the volume of mixture discharged. Since the gas delivered is constant, the decrease must take place entirely in the quantity of air injected. This results in turn in a smaller proportion of air in the mixture in the case of the 1/32 in. depth of port.

A further decrease in depth apparently changes the character of flow through the port (which has now become an imperfect orifice) in such a way as to decrease the flow further as the port approaches more completely the form of a true sharp edged orifice in which the length of the channel is zero. Such an effect is shown in figure 7 of Technologic Paper T193, referred to above.

In the absence of data on depths less than 1/32 in., the four curves of figure 8 have, therefore, been allowed to continue downward as they pass through this last point. The dotted portion of the curve for the no. 28 port shows a definite rise after passing through the transition which occurred at a somewhat greater depth. The critical ratio of depth to diameter corresponds to a somewhat deeper port as the diameter becomes larger, but, in addition to that effect, the dotted portion of the curve is also the result of a turbulent condition of flow, which will be discussed in section V.

2. BLOWING

In the case of the blowing curves in figure 5, the sharp drop from a depth of 1/16 in. to 1/32 in. shown by the no. 28 port may be explained on the basis of a transition from capillary to orifice type of flow. With the capillary type of flow the velocity at the rim of the port is very low, which permits the flame to maintain itself very near to the port. This flame in the slow-moving mixture at the port rim in effect seals the rest of the flame to the port. After the change to the orifice type of flow the boundary of the stream is no longer in contact with the walls at the exit end of the channel and its velocity is only a little less than the average velocity. There is no longer a slow-moving boundary, the burning of which keeps the flame in place, and consequently

the flame is blown off the port at much lower average velocities than before. A lower average velocity at a given gas rate necessarily means less air, both of which are found experimentally.

3. FLASH BACK

In the case of the flash-back curves of figure 6 the rising curves indicate flash back at higher and higher gas rates as the depth of the port becomes less. That is, as the port channel becomes shorter the susceptibility to flash back increases, as might be expected. The flame in the slow-moving boundary, assisted by pulsations and slight turbulence, finds it easier to creep down through the port at one side. On changing to the orifice type of flow such an opportunity may be largely removed because the boundary layer may not be moving as slowly as it does when it is in contact with the channel wall. The proportion of air in the mixture most likely to flash back remains about the same. Flash back can occur only if the velocity of flow is reduced, which requires that the gas rate be less.

V. EFFECT OF TURBULENCE ON THE FLASH-BACK AND BLOWING LIMITS AND ON THE NORMAL INJECTION OF PRIMARY AIR

Turbulence in the burner casting affects the position of some of the limits of operation of a burner. The blowing limit and the normal injection of primary air may be affected only slightly but the flash-back limit is affected markedly. This effect is naturally more pronounced as the depth of the port becomes small and its diameter large.

In this particular case the effects of turbulence made their appearance only on the no. 28 port and at depths less than ½ in. The effects are shown by the dotted curve branching from the one for the no. 28 port in figures 5, 6, and 8. In addition to the abnormal trend of the curves, the turbulence was evidenced by a vibratory motion of the flame surfaces and by an accompanying (or perhaps resulting) singing noise, which at times increased to a scream.

The term "turbulence" used in the present sense simply serves to express one of the factors which appear to cause this rather complicated phenomenon and may have little or no connection with the term as used in ordinary pipe flow. Computations disclosed the fact that at the higher rates of flow through the burner casting, indeed, at the points where "singing" began, the velocity through the casting was near to or greater than the critical velocity at which the flow becomes turbulent in a long, smooth, straight tube. In view of the relative shortness of the burner casting, however, and the various disturbing factors incident to its irregular shape, this coincidence may have little significance. The high frequency of the singing noise suggests either a vibration of the air column within the burner, or the rapid alternations of position of the flame surface itself as a source. The latter can actually be seen, and no sound is heard unless the flame is present (the flow remaining unchanged). Vibrations which may cause the pulsations in the flame may, however, originate somewhere in the burner casting.

An attempt was made to lessen the intensity of the pressure fluctuations or to damp out the turbulence, if turbulence was the direct cause, by interposing the spacer (shown in fig. 1) between the casting and the plate through which the ports were drilled.

The spacer was used in additional tests of ports which had previously shown no indication of being affected by turbulence, and the results indicated that the interposition of the spacer had no significant effect.

When used with ports with which turbulence had caused trouble, however, the spacer eliminated the difficulty almost entirely by providing more space and time for the turbulence to die out after the velocity had dropped below the critical value in the larger part of the burner head. The solid portion of the curves in figures 5, 6, and 8 below a depth of ½ in. for the no. 28 port were determined with the spacer in place.

VI. CONCLUSIONS

The effect on the position of the yellow-tips limit of burner operation when the depth of the port is varied from 1½ in. to ½₂ in. is negligible.

The effect of such changes in depth on the position of the flash-back and blowing limits is small until the depth has decreased to ¼ in., the burner being more susceptible to flash back and a very little more susceptible to lifting as the depth decreases.

Below ¼ in. the effect of decreasing the depth of the port becomes more marked, the change from ¼ in. to ⅛ in. being roughly equal to that from 1½ in. to ¼ in. The injection of primary air is limited by the resistance to flow through the ports and increases more and more rapidly as the depth decreases to ⅛ in.

Ten of the fifteen curves shown in figures 5, 6, and 8 pass through a maximum at a depth of ⅛ in., while most of the others show a change in curvature in this direction at that depth.

A port depth of ⅛ in. with the diameters of the ports studied was found by experiment to permit the largest flow at a given pressure difference, and corresponds closely to that ratio of length of channel to diameter of orifice at which the change from the channel type of flow to the orifice type occurs. This transition, in which the stream of fluid no longer fills the channel and a contraction appears is concluded to be the cause of the decreased susceptibility to flash back, the increased susceptibility to lifting, and the decrease in the injection of primary air which occurs as the depth of the port is decreased from ⅛ in. to ½₂ in.

These effects are found with natural gas as well as with the mixed gas with which most of the tests were made.

In general, these effects are the same, regardless of the size of the port, between no. 40 and no. 28.

With the no. 28 port the inability of the ports less than ½ in. deep to suppress turbulence which arises in the burner casting leads to a marked increase in susceptibility to flash back and also to blowing, as well as to a decreased injection of primary air. This turbulence was shown by computation to be the result of the flow through the casting exceeding the critical velocity, at the normal gas rate of 226 Btu per hour per port.

A study of the curves presented in this paper leads to the conclusion that some improvement in operation of burners of domestic appliances might be expected as a result of using ports ¼ in. deep, instead of less; but that little is to be gained by making them deeper than ¼ in. The uniformly adverse effects of turbulence might be avoided for the most part by increasing the cross section of the burner casting to a point where the velocity of flow will be less than the critical velocity. Otherwise, ports smaller than no. 28 or deeper than ½ in. are required to suppress the turbulence so produced in a burner such as that on which these tests were made.

WASHINGTON, January 18, 1937.

U. S. Department of Commerce National Bureau of Standards

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BOILING POINTS AND DENSITIES OF ACETATES OF NORMAL ALIPHATIC ALCOHOLS

By Mieczysław Wojciechowski [1] and Edgar R. Smith

ABSTRACT

The boiling points, rates of change of boiling point with pressure, and densities of methyl acetate, ethyl acetate, *n*-propyl acetate, and *n*-butyl acetate were measured by precise comparative methods using water as the reference standard. As in previous work on the normal saturated hydrocarbons and normal aliphatic alcohols, it was found that the introduction of each CH_2 group into the chain of a molecule containing a normal alkyl group of more than some small number *n* of carbon atoms causes *dt/dp* to increase by a constant value which is independent of the chemical nature of the molecule.

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I. METHODS OF MEASUREMENT

In previous papers it was shown that in the homologous series of normal saturated hydrocarbons [11] [2] and normal aliphatic alcohols [12], containing more than some small number *n* of carbon atoms, the addition of a CH_2 group to the normal alkyl group to form the next higher normal alkyl group results in an increase of 0.0029° C per millimeter of mercury in the coefficient *dt/dp* at the normal boiling point. Since this value was found to be independent of the chemical nature of the compound, the additivity of the effect of the CH_2 group on *dt/dp* was postulated. In this paper a similar investigation of the relation between the *dt/dp* coefficient and the molecular weight of the compound in the series of acetates of normal aliphatic alcohols is described. In addition, there are reported the boiling points and densities of the following esters: methyl acetate, ethyl acetate, *n*-propyl acetate, and *n*-butyl acetate. For determining boiling points Swiętosławski's ebulliometric technic [7] and comparative method with water as a primary standard was applied. Details of the experimental procedure for determining the boiling point and the coefficient

[1] Guest Worker from the Polytechnic Institute, Warsaw, Poland.
[2] The figures in brackets refer to references listed at the end of the paper.

dt/dp have been described briefly in the paper on hydrocarbons [11]. Temperatures were measured with a platinum-resistance thermometer having a coiled filament [4], calibrated at this Bureau and furnished by C. H. Meyers. Normal boiling points were calculated by the use of the formula previously reported [11],

$$t_s = t_s' + \frac{\Delta t_s}{\Delta t_w}(100 - t_w'),$$

where t_s represents the normal boiling point of the substance under investigation, t_s' the boiling point actually measured, and t_w' the boiling point of water actually measured under the same pressure as that of the substance. The ratio $\Delta t_s/\Delta t_w$ at 1 atmosphere was computed from boiling points of the substance and of water under the same pressure, slightly above and slightly below 1 atmosphere.

For the density measurements, the differential method of twin picnometers [5], with water as a reference liquid, was used. To control the purity of substances investigated, Świętosławski's ebulliometric test of purity and his scale for classification of the preparations were used.

II. METHOD OF EXTRAPOLATION OF THE DATA

To compute the physico-chemical constants of the pure compounds a method of extrapolation which has been reported previously [13] was used. The method is similar to that of Świętosławski [7] and is based on the correlation of the data for a given property with the purity of the preparation expressed by Δt, the difference between its boiling point and condensation temperature. This difference is a function of the nature and concentration of the impurities in a substance and is zero if the substance is pure.

Having made the measurements of Δt and of a given physico-chemical constant for a series of preparations of the same compound having different purities, as, for example, a few successive fractions of the distillate from an efficient column, one may plot Δt, the difference between the boiling point and temperature of condensation of each of the preparations, in a differential ebulliometer, against the data obtained for the given constant. Direct extrapolation of the curve to the point where Δt equals zero gives the constant corresponding to the pure substance or azeotropic mixture. If only one impurity is present, Δt is a very nearly linear function of its concentration, and so is the value of any property measured. Hence the relation between Δt and the given property is also very close to linearity. When there are several impurities, which generally is the case, and their concentration is different in each fraction of the distillate, Δt, as well as the property measured, is expressed by a curve whose slope and curvature depend on the nature and concentrations of the impurities. In general, the relation between Δt and the property measured may be expressed by a curve. However, as the degree of purity of the substance investigated becomes higher, the curvature decreases, and for preparations whose purity is such that Δt is only a few thousandths of 1 degree, it becomes nearly linear, thus permitting a reliable extrapolation to $\Delta t = 0$.

III. PURIFICATION OF MATERIALS

The best grades of substances that could be purchased were purified by distillation through an efficient 40-bulb column of the Świętosławski type. Esters are difficult to maintain in a state of high purity, because they are very hygroscopic and readily hydrolyze on boiling. Preparations for the determination of boiling point and related properties were distilled directly into the ebulliometer to avoid contact with moist air. Only fractions distilling at constant temperature, as an evidence of their purity, were taken for measurement. A minute amount of water in the ebulliometer, mostly as water adsorbed on glass, may have slightly contaminated the preparations, but its effect was not differentiated from the effects of traces of other impurities.

1. METHYL ACETATE

Three liters of the best available methyl acetate, reagent grade, was distilled, and only the middle fraction, which distilled practically at constant temperature, was collected. The preparation thus obtained was of the fourth degree of purity on Świętosławski's scale, having Δt equal to 0.014° C.

2. ETHYL ACETATE

A preparation of the fifth degree of purity, having $\Delta t = 0.003$, was obtained, but during the determination of its boiling point Δt increased to 0.007° C. To calculate the true normal boiling point of ethyl acetate it was assumed that the initial difference Δt, as well as the increase of Δt to 0.007° C, was caused by water. To measure the change of boiling point corresponding to such an increase of Δt when caused by water, a small amount of a freshly prepared solution of water in ethyl acetate of the same purity was added to that in the ebulliometer. In this way the correction of boiling point for impurity was determined experimentally.

3. *n*-PROPYL ACETATE

The middle fraction of the distillate was of high purity, characterized by a Δt of 0.004° C.

4. *n*-BUTYL ACETATE

Distillation through the column yielded two preparations of the fourth degree of purity expressed by $\Delta t = 0.007°$ and 0.015° C.

IV. EXPERIMENTAL RESULTS AND CONCLUSIONS

The data obtained for the boiling points of four acetates of normal aliphatic alcohols are given in table 1.

TABLE 1.—*Boiling point data for four esters*

Substance	Δt	Normal boiling point	Normal boiling point extrapolated
	°C	°C	°C
Methyl acetate	0.014	56.32₃	
Ethyl acetate	.003	77.11₃	77.11₄
n-Propyl acetate	.004	101.54₃	
n-Butyl acetate	.007	126.10₃	126.09₄
	.015	126.11₄	

Table 2 contains the values of dt_s/dt_w, the ratio of change of boiling point of each substance to the change of the boiling point of water caused by a small increment of pressure, and values of dt/dp, the increment of boiling point per millimeter of change of pressure. The values in parentheses were obtained by interpolation.

TABLE 2.—*Data for dt/dp coefficients for four esters*

Substance	$\frac{dt_s}{dt_w}$	Boiling point of water	$\left(\frac{dt}{dp}\right)_{p=760}$	Difference
		°C	°C/mmHg	
Methyl acetate	1.0095	101.201	0.0373	
	(1.0084)	100.000		
	1.0066	98.216		
				0.0028
Ethyl acetate	1.0856	101.207	.0401	
	(1.0849)	100.000		
	1.0837	97.853		
				.0029
n-Propyl acetate	1.1678	100.910	.0430	
	(1.1642)	100.000		
	1.1567	97.932		
				.0026
n-Butyl acetate	1.2356	100.517	.0456	
	(1.2346)	100.000		
	1.2296	97.511		

The data for dt_s/dt_w permit one to calculate the correction for normal boiling points of the substances, within the pressures expressed by the reported boiling points of water. They may serve also to compute the value of dt/dp corresponding to any pressure within the reported limits, by the use of the equation

$$\left(\frac{dt}{dp}\right)_s = \frac{dt_s}{dt_w} \cdot \left(\frac{dt}{dp}\right)_w$$

Data for the densities of the esters investigated are given in table 3.

[3] $(dt/dp)_w = 0.03685°/mm$. L. B. Smith, F. G. Keyes, and H. T. Gerry, Proc. Am. Acad. Arts Sci. 69, 137 (1934); N. S. Osborne and C. H. Meyers, J. Research NBS 13, 1 (1934) RP691.

TABLE 3.—*Data for densities of the esters at 25° C*

Substance	Δt	Density	Average	Density extrapolated
	°C	g/ml	g/ml	g/ml
Methyl acetate	0.014	0.92741 .92722	0.927	0.927
Ethyl acetate	.003	.89464 .89471	.89468	.8946
n-Propyl acetate	.004	.88297	.88297	.8830
	.011	[1] .88286 [2] .88286	.88286	
n-Butyl acetate	.007	.87632	.87632	.8763
	.015	.87627	.87627	

Table 4 contains a comparison of the authors' data with some previously reported.

TABLE 4.—*Comparison of the data of the present work with results reported in the literature*

Substance	Author	Boiling point	$\left(\frac{dt}{dp}\right)_{p=760}$	d^{25}_4
Methyl acetate	E. Beckmann and P. Fuchs [2]	57.4	0.0376	
	S. Young and G. L. Thomas [14]	57.1		
	S. Young [15]	57.1		
	J. H. Mathews [3]	57.0 to 57.2		
	M. Wojciechowski and E. R. Smith	56.32	.0373	0.927
Ethyl acetate	S. Young and G. L. Thomas [14]	77.15	.0380	
	E. Beckmann and P. Fuchs [2]	76.5	.0468	
	J. Timmermans [8]	77.15		
	J. Timmermans and Hennaut-Roland [9]	77.15		.89453
	C. P. Smyth and W. S. Walls [6]	76.7 to 76.9		.8943
	J. H. Mathews [3]	77.06		
	M. Wojciechowski and E. R. Smith	77.11	.0401	.8946
n-Propyl acetate	S. Young and G. L. Thomas [14]	101.55	.0440	
	E Aries [1]	101.7		
	J. H. Mathews [3]	101.35 to 101.6		
	M. Wojciechowski and E. R. Smith	101.55	.0430	.8830 [4]
n-Butyl acetate	E. R. Washburn and C. H. Shildneck [10]	125.8	.08	.8769
	M. Wojciechowski and E. R. Smith	126.09	.0456	.8763

From table 2 it is obvious that in the case of acetates the introduction of each CH_2 group into the chain of a molecule causes an increase of the dt/dp coefficient by a substantially constant value, the average for the esters investigated being equal to 0.0028. This increment agrees with that measured for a series of normal saturated hydrocarbons [11] and normal aliphatic alcohols [12].

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